SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PHTHALOCYANINE-CONTAINING POLY(NORBORNENES)

by

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ABSTRACT

Two zinc(II) and palladium(II) phthalocyanines substituted with four norbornyl-methoxy moieties have been synthesized. These macrocycles undergo ring opening metathesis polymerization (ROMP) with norbornene or *exo*,*exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo-[2.2.1]hept-2-ene to give the corresponding poly(norbornene)s or poly(7-oxanorbornene)s. All the polymers have been characterized with NMR and UV-Vis spectroscopy, gel permeation chromatography, and thermogravimetric analysis. As shown by absorption and fluorescence spectroscopy, the phthalocyanine ring in the poly(norbornene)s, in particular for the palladium(II) system, probably due to the higher solubility and lesser extend of cross linking. The photophysical properties of these phthalocyanine-containing polymers have also been studied using steady-state and transient spectroscopy. Due to the heavy atom effect, palladim(II) phthalocyanine-containing polymers show only a very weak fluorescence and a higher quantum yield of intersystem crossing than those of the zinc(II) analogues.

An unsymmetrical zinc(II) phthalocyanine with one norbornene substituent has also been prepared and converted to poly(norbornens) and poly(7-oxanorbornenes) using similar methods. Having only one norbornene moiety, this monomer gives less cross-linked polymers, giving higher fluorescence quantum yields when compared with the respective tetrasubstituted analogues. Fluorescence quenching of these polymers has also been performed using 1,4-naphthaquinone as the quencher. I has been found that the rate of quenching is faster for lower-molecular-weight polymers. Having ester functionalities, **43** and **44** undergo alkaline hydrolysis to give the corresponding water-soluble polymers **45** and **46**, respectively, which are highly aggregated in water as shown by UV-Vis spectroscopy.

摘要

合成了兩類帶有四個甲氧基降冰片烯基的酞菁鋅(II)和酞菁鈀(II)化合物，這些大分子化合物與降冰片烯或 exo,exo-5,6-二(甲酸甲酯基)-7-氧-二環[2.2.1]-2-庚烯通過易位聚合的方法，得到相應的聚降冰片烯或聚(7-氧降冰片烯)。所有的聚合物均通過核磁共振、紫外-可見吸收光譜，凝膠滲透色譜和熱重分析表征。吸收和螢光光譜證實，帶有降冰片基的酞菁化合物，特別是酞菁鈀(II)體系，存在極強的聚集作用，而帶有聚(7-氧降冰片烯)基的酞菁化合物的聚集作用則降低，可能是由於後者的較高的溶解度和較低的交聯作用。通過穩態和瞬態光譜的方法研究了這些帶有聚合物的酞菁化合物的光物理特性。由於重原子效應，帶有聚合物的酞菁鈀(II)與酞菁鋅(II)化合物相比具有較弱的螢光和較高的量子產率。

合成了帶有一個降冰片烯基的不對稱酞菁鋅化合物，並用相似的方法將其轉化爲相應的聚降冰片烯和聚(7-氧降冰片烯)化合物。由於只帶有一個降冰片烯取代基，這些單體通過聚合後得到低交聯程度的聚合物，他們與相應的帶有四個取代基的化合物相比具有較高的螢光量子產率。用 1,4-萘醌作爲猝滅劑研究了這些聚合物的螢光猝滅作用。發現低份子量的聚合物的猝滅速率較快。帶有酯基的化合物 **43,44** 通過鹼性水解分別得到相應的水溶性的化合物 **45,46**，從紫外-可見吸收光譜發現他們在水中具有較高的聚集作用。

ACKNOWLEDGMENT

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ABBREVIATIONS

General:

AcOH	Acetic acid
AIBN	2,2'-Azobisisobutyronitrile
t-Bu	*tert*-Butyl
Cy	Cyclohexyl
DBU	Diazabicyclo[5.4.0]undec-7-ene
DMF	*N*,*N*-dimethylformamide
DMSO	Dimethyl sulfoxide
DPBF	1,3-Diphenylisobenzofuran
equiv.	Equivalent
GPC	Gel permeation chromatography
h	Hour(s)
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
Me	Methyl group
M_n	Number-average molecular weight
MO	Molecular orbital
M_w	Weight-average molecular weight

OAc	Acetate
PDI	Polydispersity index
Ph	Phenyl
ROMP	Ring opening metathesis polymerization
r.t.	Room temperature
TAS	Transient absorption spectroscopy
TCSPC	Time correlated single photon counting technique
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-visible

Nuclear Magnetic Resonance (NMR):

$\{^1H\}$	Proton decouple
δ	Chemical shift
d	Doublet
J	Coupling constant
m	Multiplet
q	Quartet
s	Singlet

t	Triplet

Mass Spectrometry (MS):

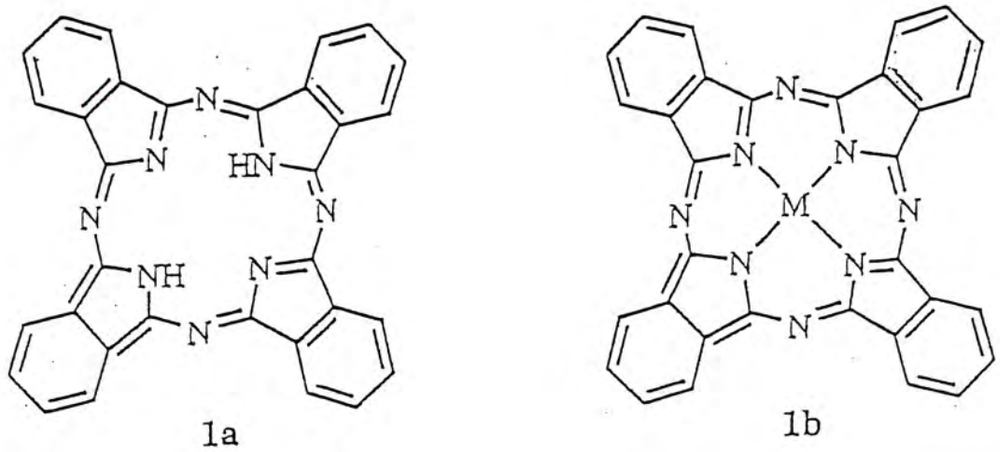
m/z	Mass / charge
MALDI-TOF	Matrix-assisted laser desorption/ionization time of flight
EI	Electron impact
LSI	Liquid secondary ion

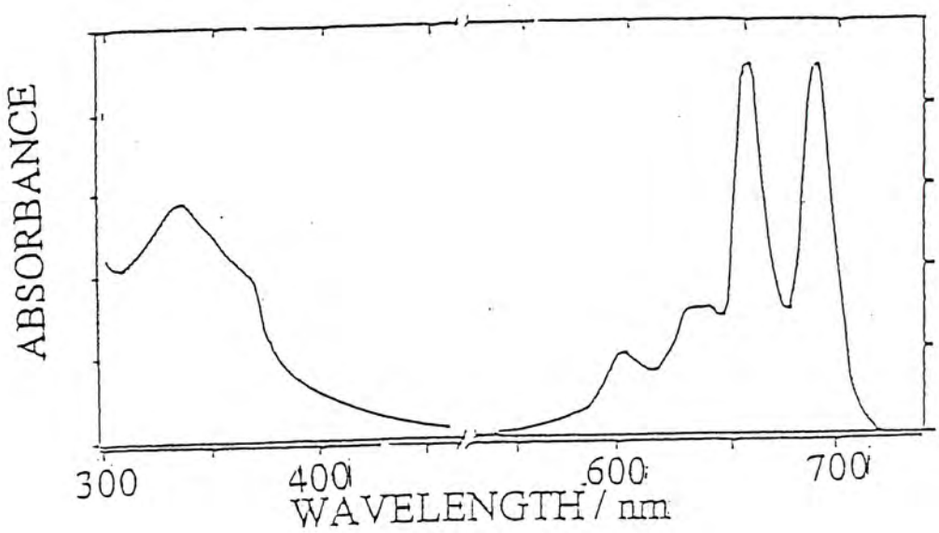
1. INTRODUCTION

1.1 General Background of Phthalocyanines

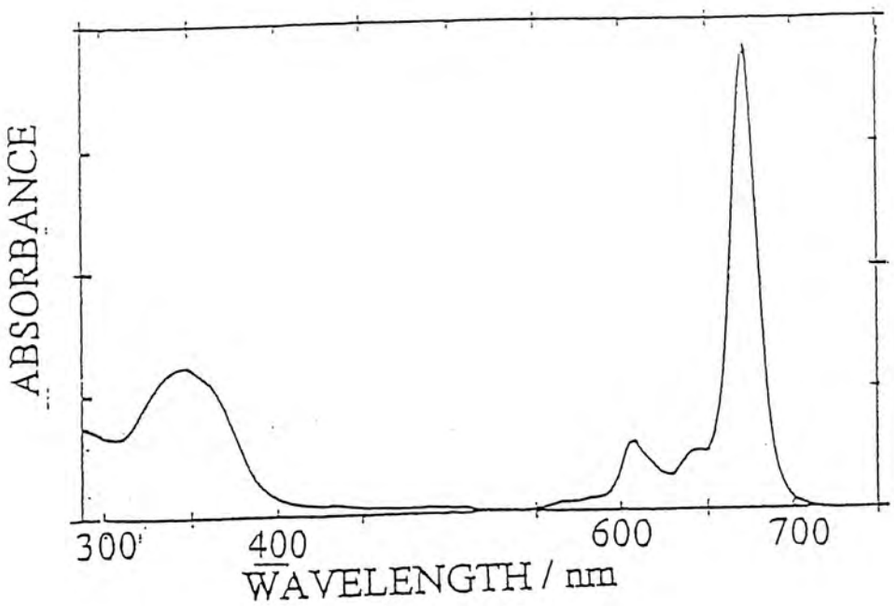
Phthalocyanine was first discovered in 1907 as a by-product during the preparation of *o*-cyanobenzamide from phthalamide and acetic anhydride.[1] The structure of this novel macrocyclic compound remained unknown until Robertson *et al.* who determined the structure about thirty years later.[2] To date, a vast number of phthalocyanines with different substituents and central metal ions have been synthesized. Due to their interesting optical and electrical properties, this class of functional dyes has found its applications in many disciplines including photosensitizers,[3] sensors,[4] electrochromic displays,[5] and conducting materials.[6]

Phthalocyanine **(1a)** and its metal derivatives **(1b)** contain a highly delocalized π system. They absorb strongly in the far-red end of the visible region (670 - 720 nm) giving a characteristic blue or green color. Figure 1 shows the UV-Vis spectra of a general metal–free and metallophthalocyanine.[7] Due to a lowering in symmetry from D_{4h} to D_{2h}, the Q band at *ca.* 680 nm observed for metallophthalocyanines (Fig. 1b) is split for metal-free phthalocyanines (Fig. 1a). The B band or Soret band appears at *ca.* 340 nm in both cases. The weak absorptions near the Q band can be attributed to the vibronic bands.





(a)



(b)

Figure 1. UV-Vis spectra of a general (a) metal-free phthalocyanine and (b) metallophthalocyanine.

Figure 2 shows a qualitative molecular orbital diagram which can explain the origin of two absorption bands of metallophthalocyanines.[7] The Q band arises from the transition from HOMO to LUMO (i.e. from a_{1u} to e_g) while the Soret band arises from the transition from a_{2u} to e_g. The energy of the Q band is susceptible to the effects of both the central metal ion and the substituents of the macrocyclic ring with a typical extinction coefficient of *ca.* 10^5 mol^{-1} dm^3 cm^{-1}.

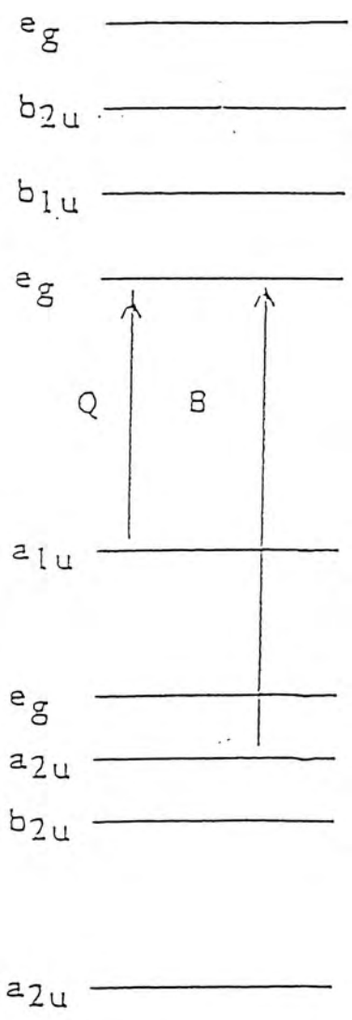


Figure 2. Qualitative MO diagram showing the two typical π-π* transitions in metallophthalocyanines.[7]

Figure 3 shows a modified Jablonski diagram illustrating the different pathways of photophysical processes. The excited states can be relaxed by a radiative transition (fluorescence and phosphorescence) or a non-radiative transition (internal conversion and intersystem crossing). According to the spin selection rule, the spin transition which involves a change in multiplicity will be forbidden. Intersystem crossing is thus a forbidden transition. However this restriction can be relaxed by the presence of heavy atom and this is known as the "heavy atom effect". Since the transition from triplet to singlet is spin forbidden, the lifetime of the triplet state is longer than that of the singlet state. This represents an important parameter in many applications.

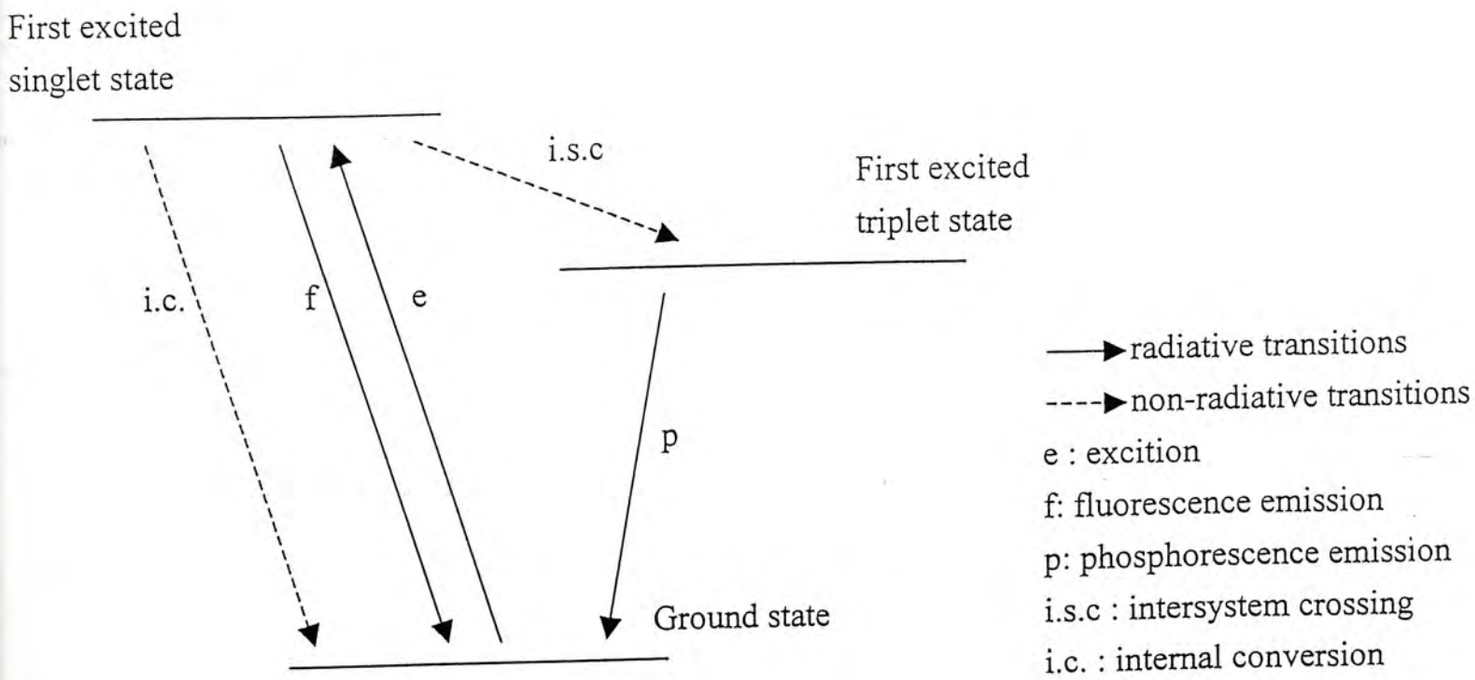


Figure 3. Modified Jablonski diagam.

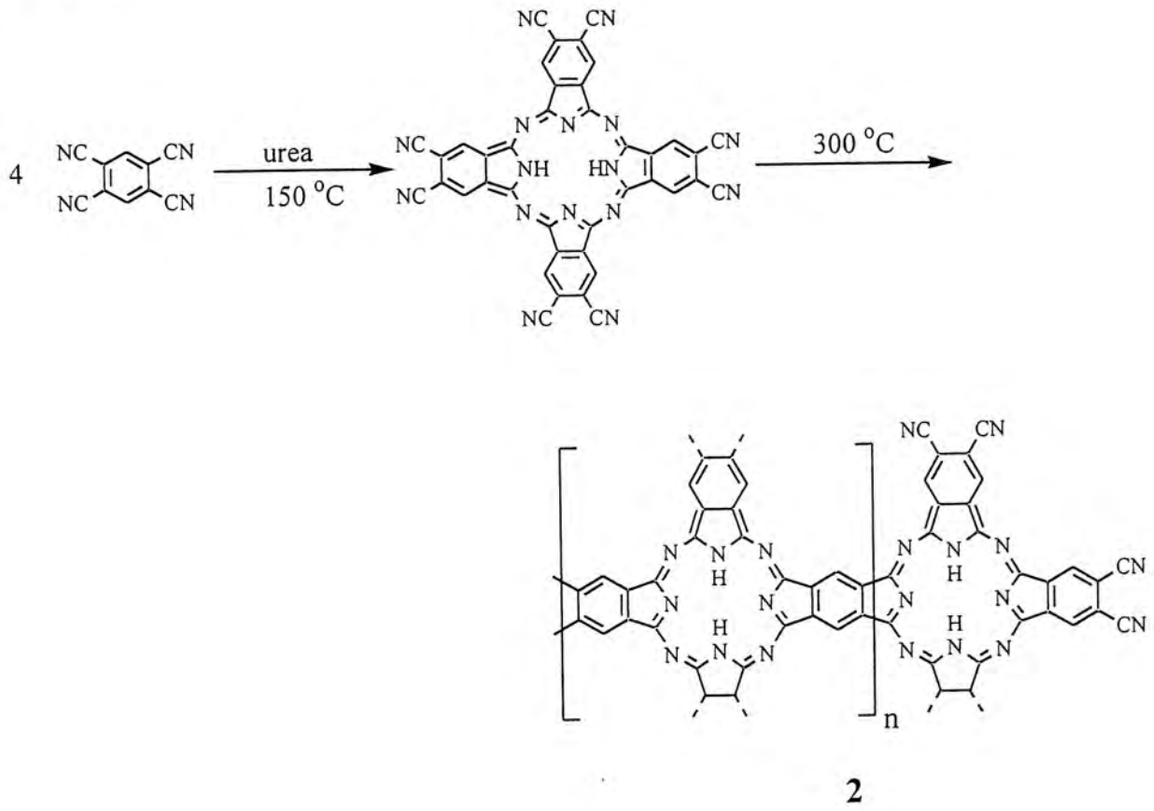
1.2 Previous Examples of Phthalocyanine-containing Polymers

Polymers are important materials for many applications. Due to the unique nature, phthalocyanines, after being incorporated into polymers, may exhibit very different properties. By systematic variation of the structure of phthalocyanines and the polymer backbones, polymeric materials with novel properties may be obtained. This section reviews the different kinds of phthalocyanine-containing polymers which have appeared in literature.[8, 9]

1.2.1 Poly(phthalocyanines) Linked Via Peripheral Substituents

Phthalocyanines are generally prepared by tetracyclization of dicyanobenzenes. Thus treatment of 1,2,4,5-tetracyanobenzene with urea at high temperature leads to the formation of network polymer **2**,[10] via the octacyanophthalocyanine (Scheme 1). As expected, most of these network polymers are insoluble in common organic solvents and at most have limited solubility in concentrated sulfuric acid. These polymers are sheet-like materials exhibiting a high degree of π-conjugation. As a result, a high conductivity can be achieved. Unfortunately, the degree of polymerization for these polymers is usually low. Only five to seven phthalocyanine rings can be linked up together in this fashion.

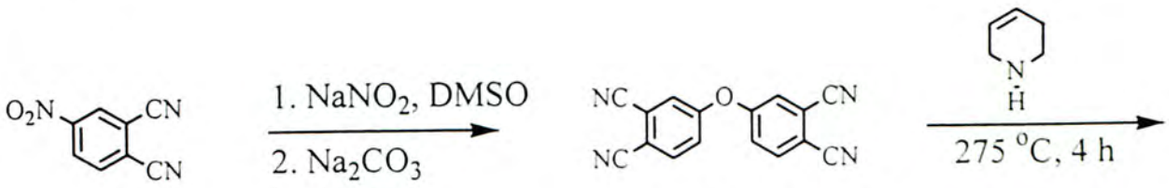
Scheme 1



2

By introducing a spacer between the phthalocyanine rings, the degree of polymerization of the polymers can usually be increased. Scheme 2 shows the preparation of the poly(phthalocyanine) **4**, which has oxo-linkers. Polymerization of the precursor **3**, which can be prepared by treating 4-nitrophthalonitrile with sodium nitrite in DMSO followed with sodium carbonate, gives the polymer **4** with a molecular mass of 18,000 to 27,000 depending on the polymerization time.[11]

Scheme 2



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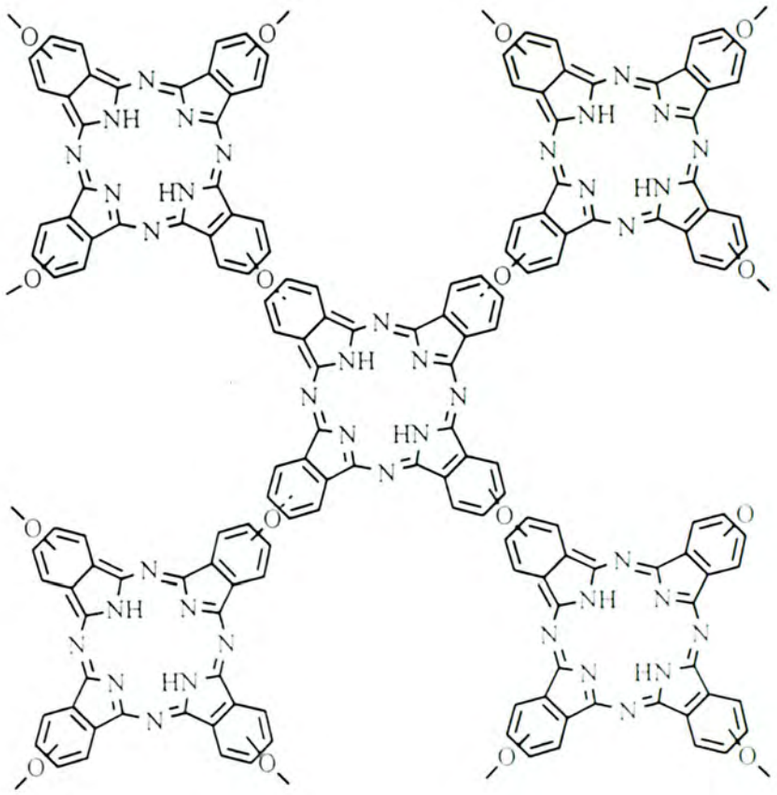

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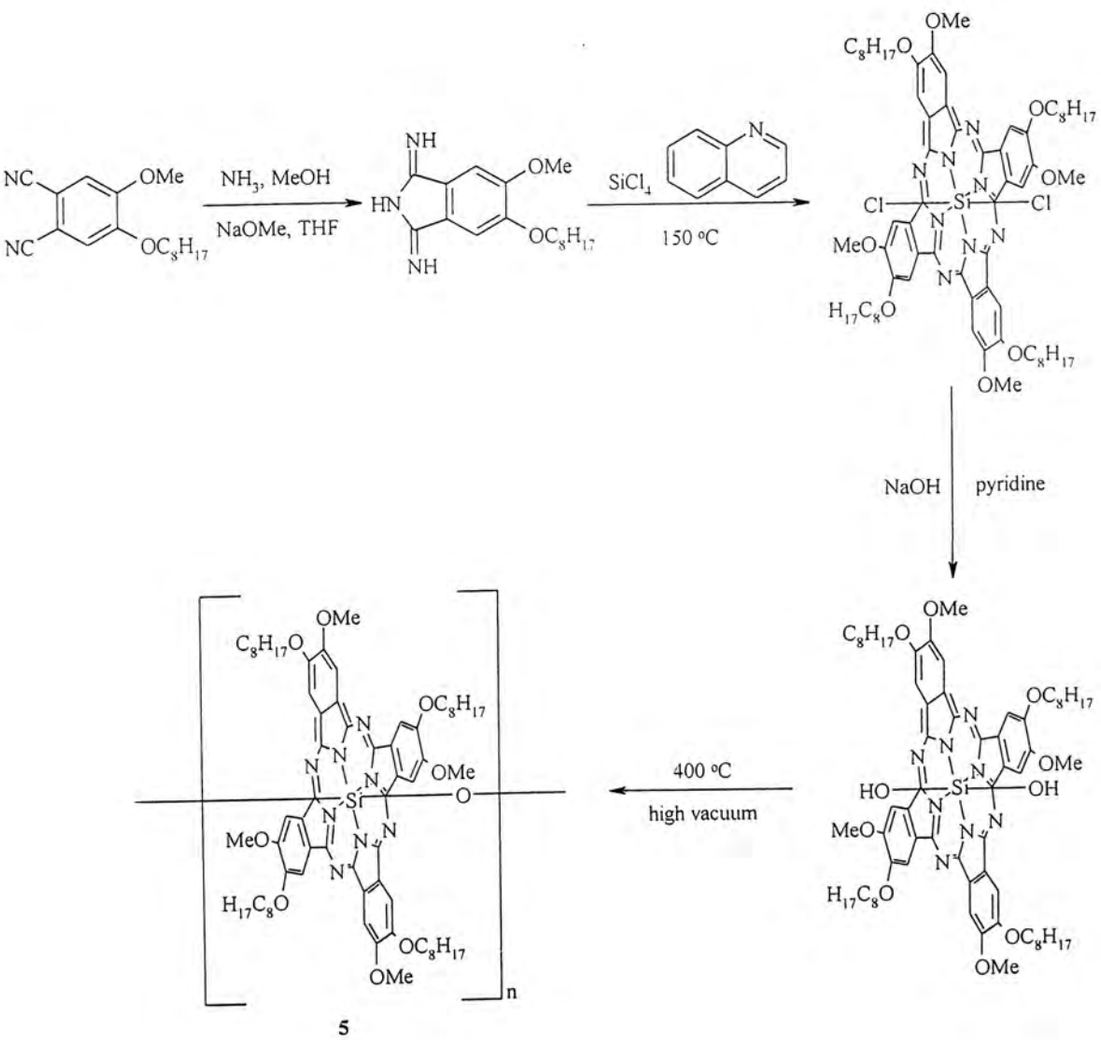
1.2.2 Poly(phthalocyanines) Linked Via Axial Ligation

This type of polymeric phthalocyanine is linked by the axial ligands attached to the central metal ion. Due to the fact that the phthalocyanine rings are skewed with each other, these polymers are also termed as *shish-kebab* polymers.[6] Most of these polymers are highly ordered in which the macrocycles are tightly held together. Most of the studies have been focused on

polysiloxanes, in which silicon phthalocyanines are linked by covalently bonded oxygen atoms. This results in the formation of rigid rod-like polymers with interesting electronic properties. An example of polysiloxanes, polymer **5**, is shown in Scheme 3.[12] The preparation involves the dehydration of (phthalocyaninato)silicon dihydroxide at 400 °C.[13] The number of repeating unit of this polymer ranges from 50 to 500 depending on the reaction time. The usage of bulky substituents such as octyloxy chains can enhance the solubility of this polymer in common organic solvents.

Scheme 3



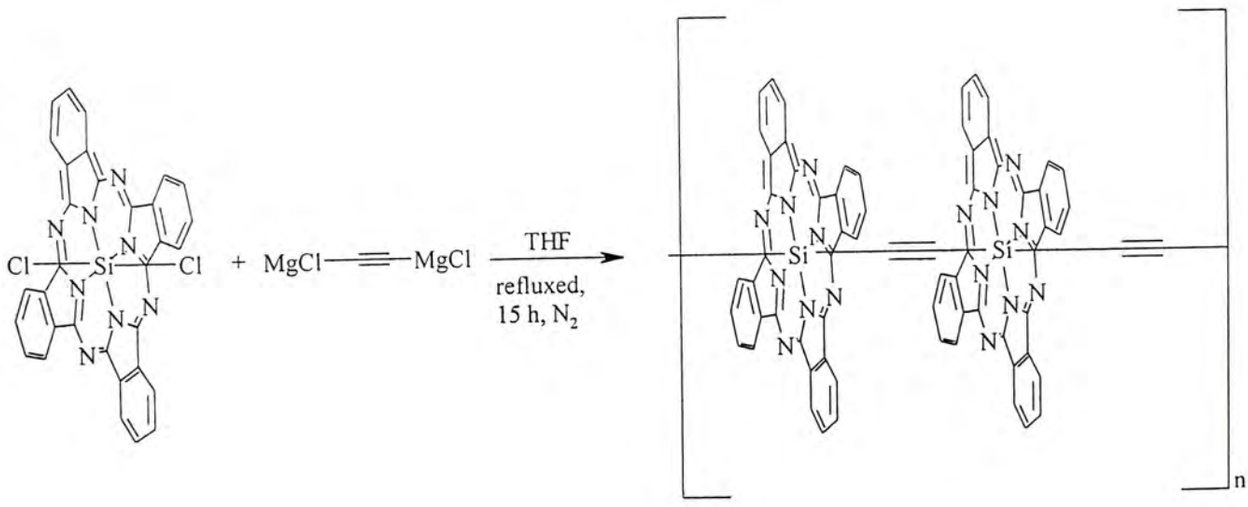
5

$n \approx 50 - 100$

Dihydroxy silicon(IV) phthalocyanine can also undergo polymerization by the treatment with excess diols, diphenols, dicarboxylic acids or dithiophenols to give polymers with bisalkoxy, bisphenoxy, bisesters and bisphenylthio derivatives as the linkers respectively.[14, 15]

Apart from these linkers, an ethynyl group can also be used as a bridge to link up silicon phthalocyanines.[16] Thus treatment of dichloro(phthalocyaninato)silicon(IV) with ethynyl Grignard reagent gives the polymer **6** (Scheme 4). The UV-Vis spectrum of this ethynyl-bridged polymer resembles that of the starting material suggesting that there are no significant π-π interactions between the orthogonally disposed phthalocyanine rings and the ethynyl bridges.

Scheme 4

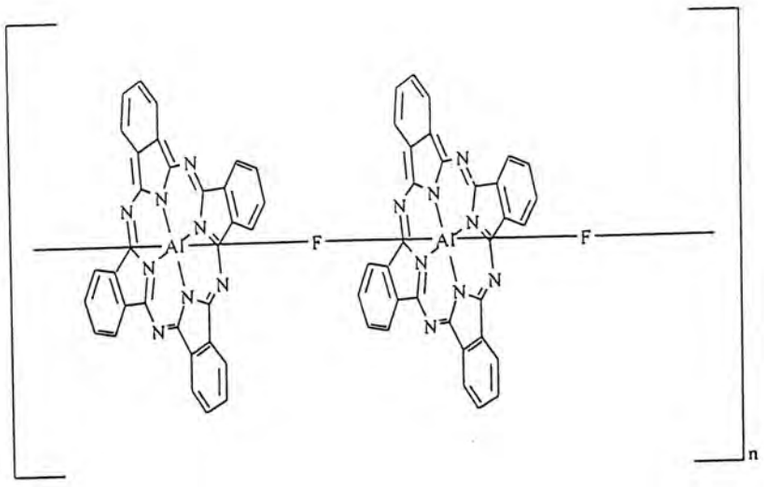


6

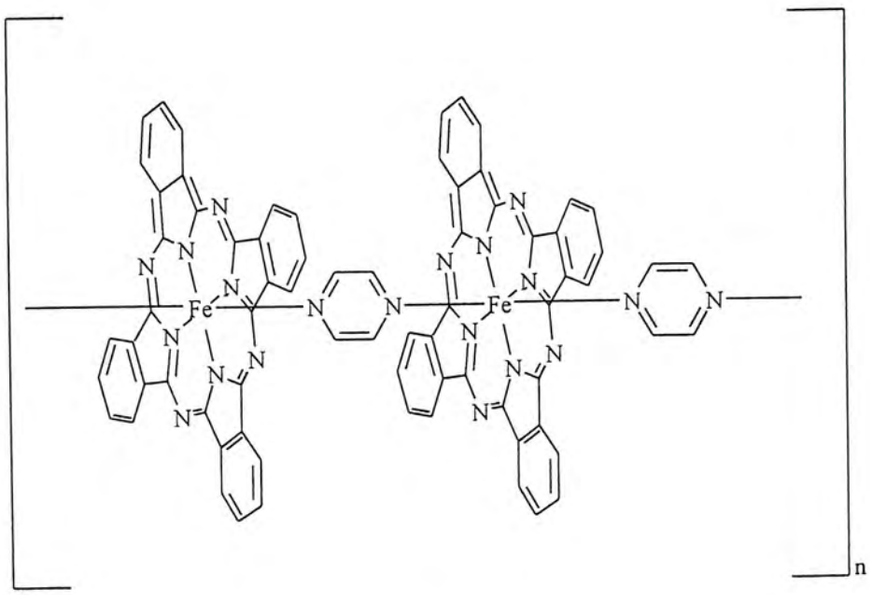
$n \approx 50$

Another example of this type of polymers contains one σ-bond and one coordinative bond to the metal ion in the main chain. Aluminum or gallium phthalocyanines, when covalently bound to a small and highly electronegative ion like fluoride, have a high tendency to link up together by Lewis acid-base interactions (e.g. 7).[17] Polymer 7 can form needle-like crystallites after being purified by repeated sublimation at 510 – 530 °C and gives a broad UV-Vis spectrum in which the Q band is significantly blue-shifted.[18]

Metallophthalocyanines can also be linked up with bidentate ligands to form one dimensional polymers. Iron, ruthenium, and manganese ions, which favor octahedral coordination, are commonly used, whereas typical bidentate ligands include pyrazine and piperidine. Polymer **8** is a typical coordination polymer which can be prepared directly by heating iron phthalocyanine with pyrazine in a high-boiling solvent such as glycol. The electrical conductivity of these polymers was found to be greatly increased upon treatment with oxidizing agents such as iodine, bromine, or nitrosonium salts.[19]



7



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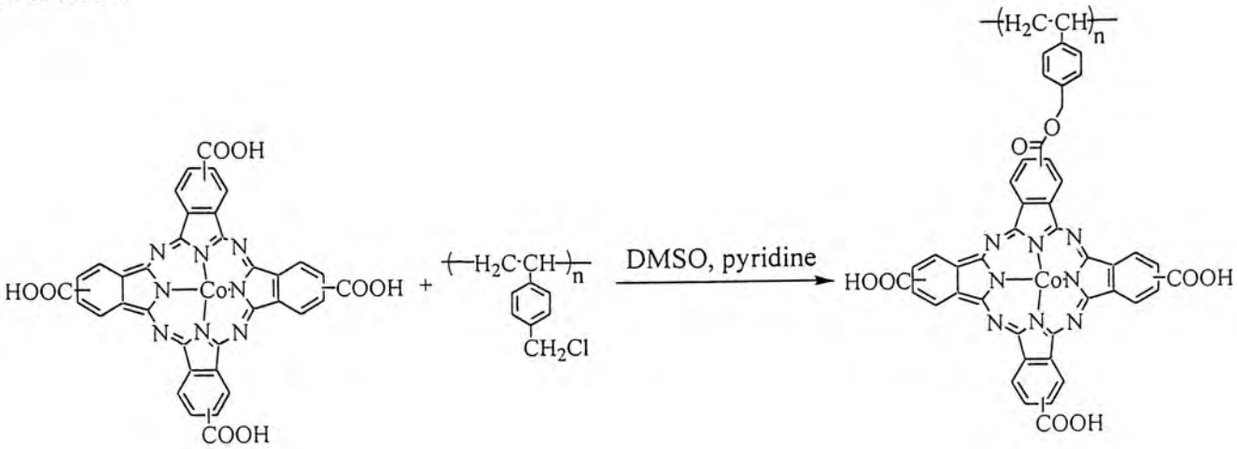
1.2.3 Poly(phthalocyanines) Attached Laterally to a Polymer Backbone

This kind of polymeric phthalocyanines can be prepared by grafting phthalocyanines to a preformed polymer. For example, treatment of cobalt(II) phthalocyanine **9** with chloromethylated polystyrene in DMSO / pyridine gives the polymeric phthalocyanine **10** (Scheme 5).[20] The use of this polymer as a photosensitizer for the reduction of methylviologen by visible light has been reported.[20]

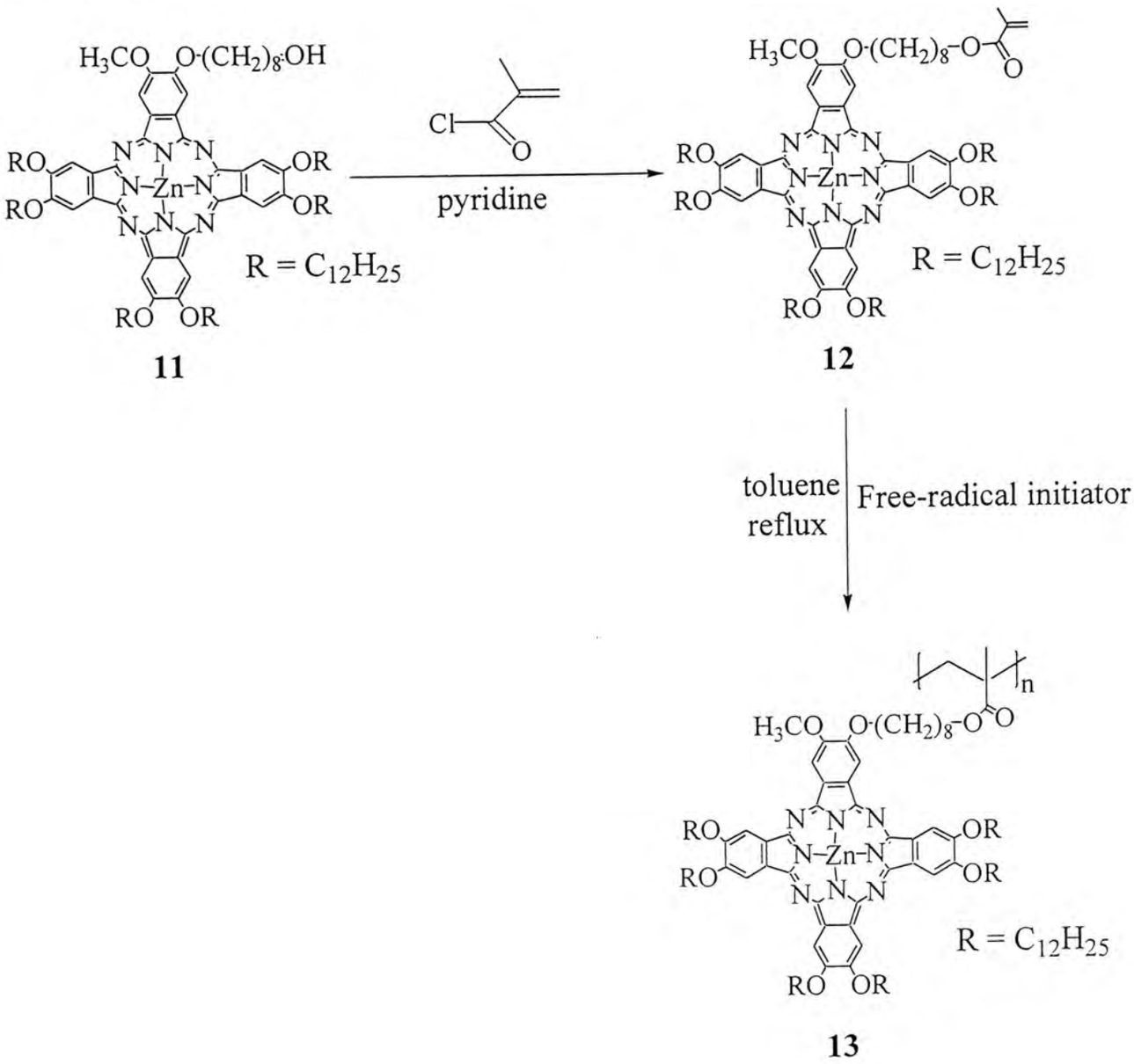
Scheme 5



9 **10**

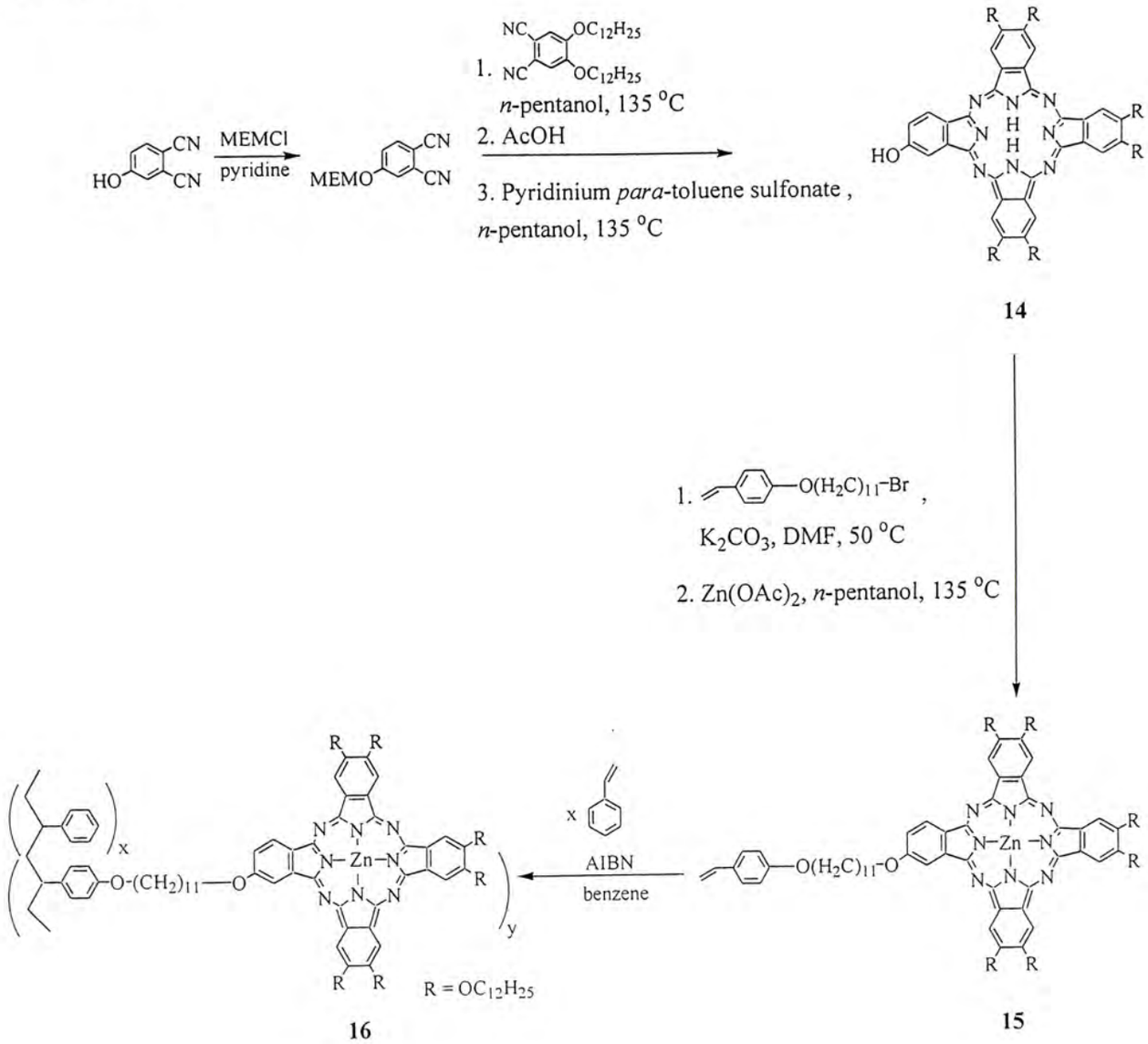
An alternative approach to this kind of polymers involves the polymerization of phthalocyanine-containing monomers. As shown in Scheme 6, reaction of the unsymmetrical phthalocyanine **11** with methacryloyl chloride gives the monomer **12**.[21] A long alkyl spacer is added between the phthalocyanine ring and the methacrylate group to minimize the steric effect which may hinder the polymerization process. Polymer **13** can be prepared from **12** by a typical free-radical polymerization (Scheme 6).

Scheme 6



Recently, McKeown *et al.* have prepared several phthalocyanine-containing polystyrenes.[22] The monomer **15**, which can be prepared from 4-hydroxyphthalonitrile in 6 steps, undergoes a radical co-polymerization with sytrene to give the polymer **16**.

Scheme 7



The UV-Vis spectra of **15** and **16** in toluene are shown in Figure 4. The former shows typical absorptions for non-aggregated phthalocyanines. However, the Q band shifts significantly from 690 to 620 nm for polymer **16**, showing that the aggregation of the macrocycles is important in this polymeric system.

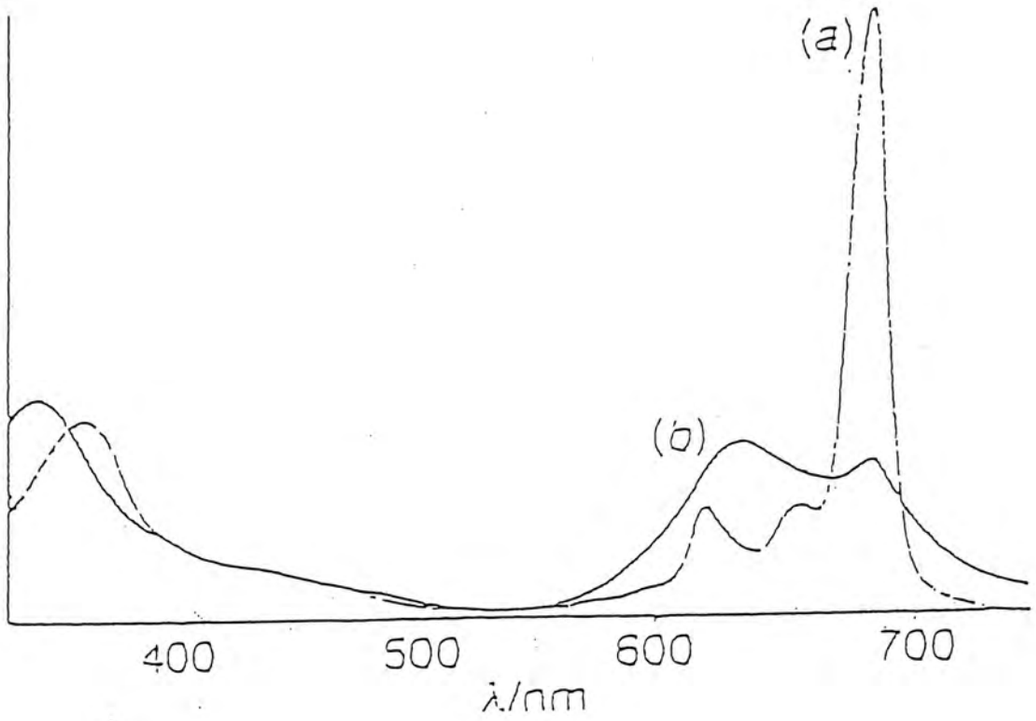


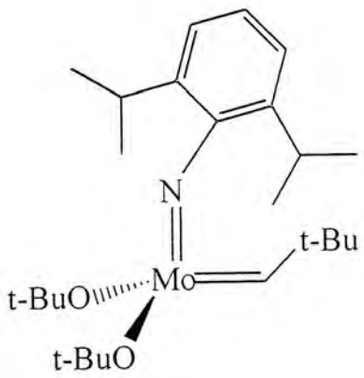
Figure 4. UV-Vis spectra of the phthalocyanine (a) monomer **15** and (b) polymer **16** in toluene.[22]

1.3 Ring Opening Metathesis Polymerization (ROMP)

Ring opening metathesis polymerization (ROMP) has received much attention since it was discovered in the 1960s.[23] ROMP is thermodynamically favored for 3-, 4-, 8- and higher membered cycloalkenes. The polymerization of 5-, 6-, and 7-membered rings depends on other physical factors such as monomer concentration, temperature, and pressure, and chemical factors such as the nature of the substituents and their positions in the ring. For bicyclic compounds, there is a high tendency to undergo a ring opening metathesis polymerization because of the high strain energy which normally gives a negative ΔG value.[24]

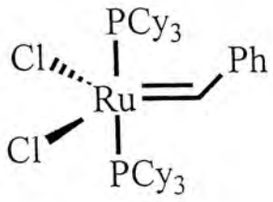
In 1968, Oshika and Tabuchi reported the polymerization of norbornene using $MoCl_5$, WCl_6, and $ReCl_5$ as the catalysts.[25] The reactions were performed in carbon tetrachloride and it was found that the yields varied with the temperature.

In 1980s, Schrock *et al.* reported a new molybdenum carbene complex which can polymerize various norbornene derivatives to give the corresponding polymers in high yield and with low polydispersity index (1.05 – 1.24).[26] Such catalyst, however, still has some disadvantages. Due to the air sensitivity, this catalyst must be stored and used under nitrogen. The polymerization by this catalyst is also sensitive to moisture. Therefore the Schrock catalyst cannot be used to polymerize norbornene derivatives which contain heteroatom functionalities.



Schrock catalyst

For these reasons, Grubbs *et al.* developed a ruthenium-based catalyst.[27] The Grubbs catalyst is stable in air and can be handled easily. This catalyst can polymerize norbornenes and 7-oxanorbornenes substituted with many different functional groups, even in aqueous media.



Cy = cyclohexyl

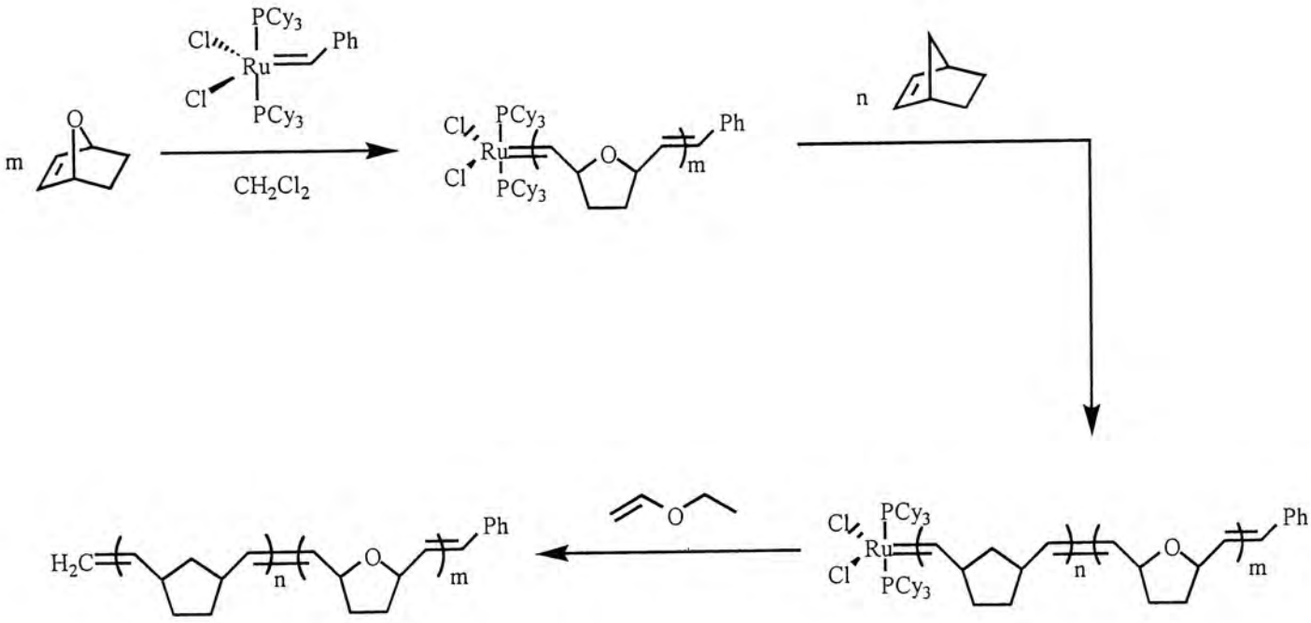
Grubbs catalyst

17

The reactivity of the Grubbs catalyst is normally higher than that of the Schrock catalyst. Tricyclohexylphosphine, being a good σ-donor, can stabilize the Ru(IV) intermediate. The two chloride substituents can also make the central metal ion more electrophilic.[28] Since the catalyst can tolerate many functional groups and can catalyze emulsion polymerization in the presence of water, it has been widely used in the past few years.

The metathesis polymerizations catalyzed by the Grubbs catalyst are living in nature. Consequently, block copolymers can be synthesized with this catalyst. Scheme 8 shows the copolymerization of norbornene with 7-oxanorbornene for exemplification. The reaction can be quenched by ethyl vinyl ether, which can terminate the reaction by breaking the Ru=C bond. The resulting Fischer-type carbene is unreactive for further reaction.

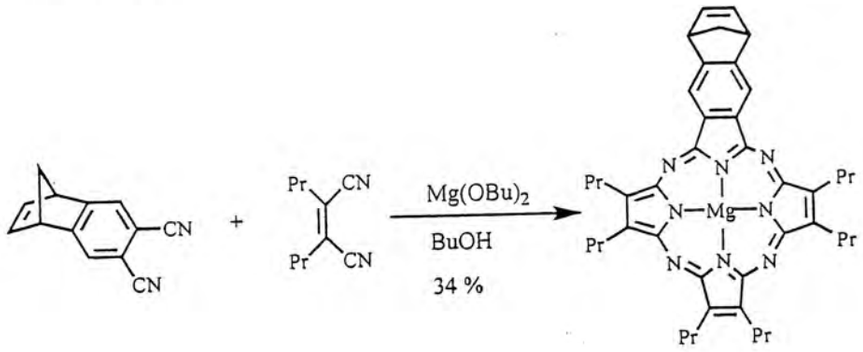
Scheme 8



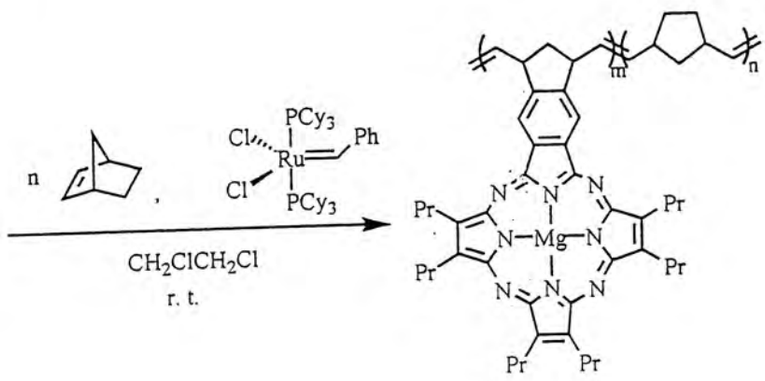
1.4 ROMP of a Norbornene-Substituted Porphyrazine

ROMP of tetrapyrrole detrivatives is extremely rare. To our knowledge, only one example has been reported recently which is illustrated in Scheme 9.[29] Treatment of the norbornene-fused phthalonitrile **18** with **19** in the presence of $Mg(OBu)_2$ leads to the formation of the unsymmetrical benzonorbornadiene derivative **20**, which undergoes a copolymerization with norbornene using the Grubbs catalyst in a degassed 1,2-dichloroethane solution. After quenching with ethyl vinyl ether, a green precipitate of **21** can be obtained.

Scheme 9



18 **19** **20**



21

$m \approx 1 - 50$

$n \approx 50 - 100$

The homopolymerization of **20** can also be carried out at higher temperature (60 °C) but only a low-molecular-weight polymer is formed in low yield, probably due to the steric hindrance.

Although substantial numbers of polymeric phthalocyanines have appeared in literature,[8, 9] none of them is prepared by the ROMP process. Photophysical properties of polymeric phthalocyanines have also been little studied. In this thesis, the preparation and photophysical properties of a new series of phthalocyanine-containing poly(norbornenes) and poly(7-oxanorbornenes) are reported.

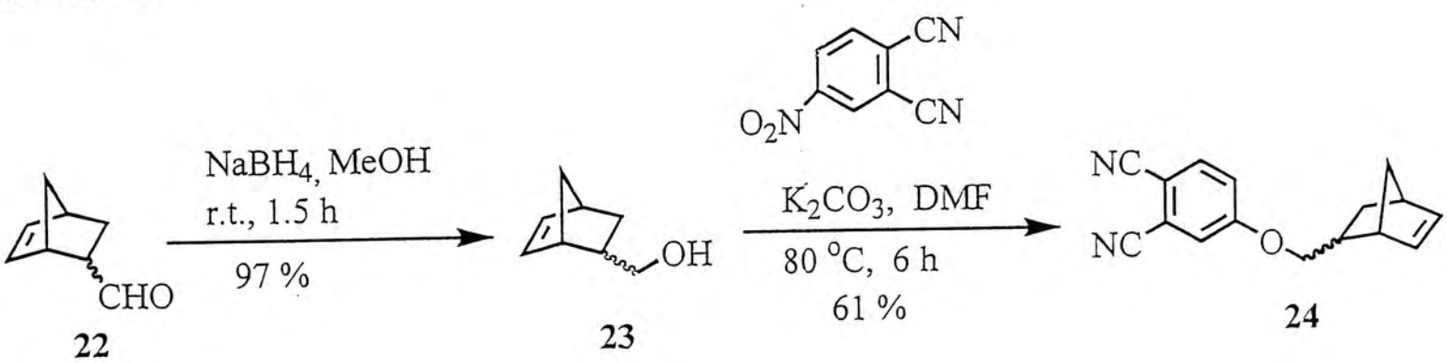
2. RESULTS AND DISCUSSION

2.1 Phthalocyanines Substituted with Four Poly(norbornene)s

2.1.1 Preparation of Tetra(norbornene) Phthalocyanines

The synthesis of phthalocyanines with norbornene substituents involves 5-norbornene-2-methanol **(23)** as the starting material, which could be obtained by reduction of the commercially available 5-norbornene-2-carboxaldehyde **(22)** (Scheme 10). To control the rate of the reaction, sodium borohydride was added to the reaction mixture in three to four portions depending on the amount of the material used. By using ten-fold excess of sodium borohydride, the reduction proceeded cleanly and the excess sodium borohydride was quenched by hydrochloric acid until the solution became slightly acidic. The ^{1}H NMR spectrum of the colorless crude product showed that it was essentially pure and contained a mixture of endo and exo isomers. Treatment of **23** with 4-nitrophthalonitrile in the presence of potassium carbonate in dry DMF afforded **24**. The color of the reaction mixture changed from yellow to brown from which compound **24** was isolated by column chromatography. White needle-like crystals were obtained after recrystallization from *n*-hexane.

Scheme 10



22 **23** **24**

As shown in Figure 5, the ^{1}H NMR spectrum of **24** in $CDCl_3$ indicates that the compound exists as a mixture of *endo* and *exo* isomers in *ca.* 1 : 4 ratio. The several downfield signals at δ 7.0 - 7.6 are due to the three aromatic ring protons. The signals at δ 5.8 - 6.1 and δ 3.5 – 3.8 can be assigned to the olefinic protons and the $-OCH_2$ protons, respectively. The remaining upfield signals are due to the norbornene protons. Figure 6 shows the $^{13}C\{^{1}H\}$ NMR spectrum of compound **24** in $CDCl_3$, which also confirms the structure of this compound. The signals at δ 73 represent the $-OCH_2$ carbon with the *exo* and *endo* isomers.

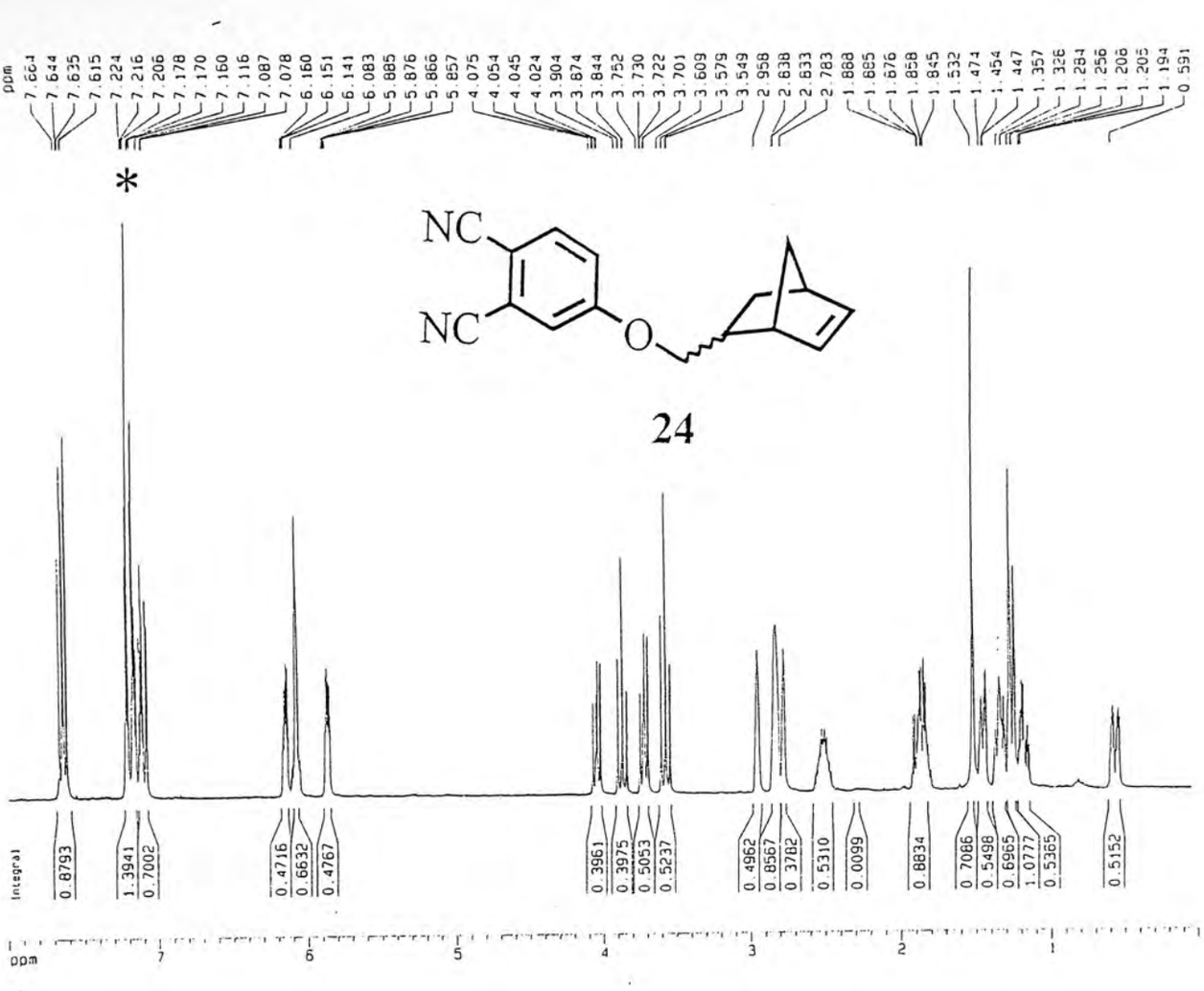


Figure 5. ^{1}H NMR spectrum of **24** in $CDCl_3$; * indicates the solvent peak.

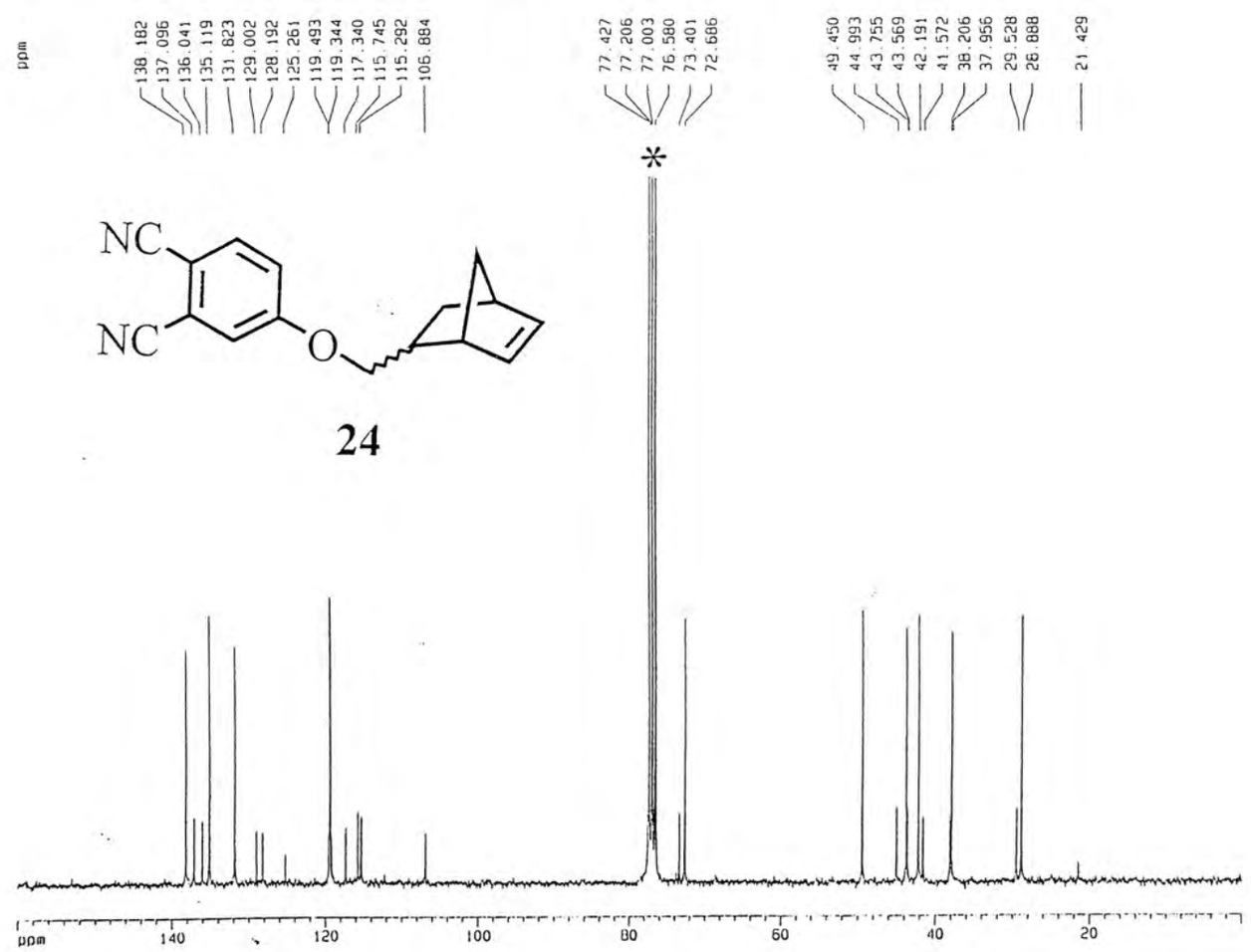
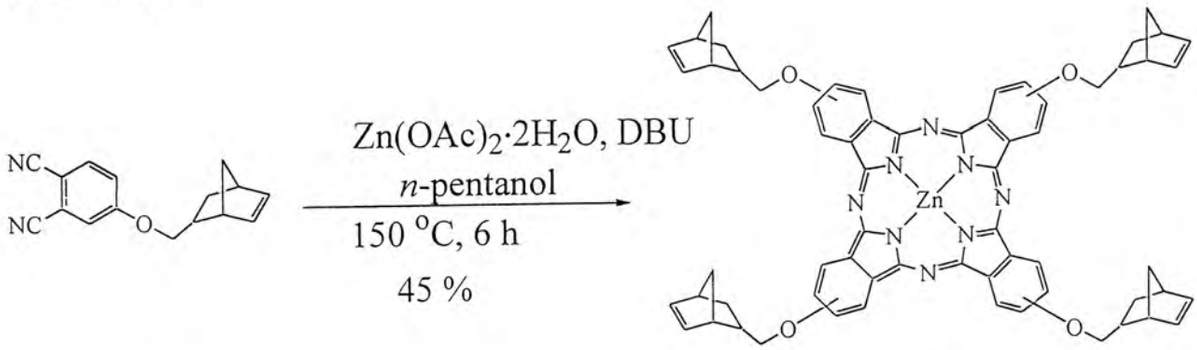


Figure 6. $^{13}C\{^{1}H\}$ NMR spectrum of **24** in $CDCl_3$; * indicates the solvent peaks.

Phthalocyanines can usually be prepared by treating the corresponding phthalonitriles with a strong base like diazabicyclo[5.4.0]undec-7-ene (DBU) and a metal salt in dry *n*-pentanol.[30] By using this methodology and $Zn(OAc)_2 \cdot 2H_2O$ as the metal salt, dinitrile **24** was converted to **25**, which contains four norbornene substituents (Scheme 11). Upon the addition of DBU at 90 °C, the color of the reaction mixture turned from yellow to green rapidly. The product was purified by column chromatography followed by reprecipitation to give a deep green solid.

Scheme 11



24 **25**

Compound **25** was characterized spectroscopically. The UV-Vis spectrum of **25** showed characteristic features for metallophthalocyanines. As shown in Figure 7, the B and Q bands appear at 337 and 676 nm respectively, while the vibronic band at 611 nm is also shown.

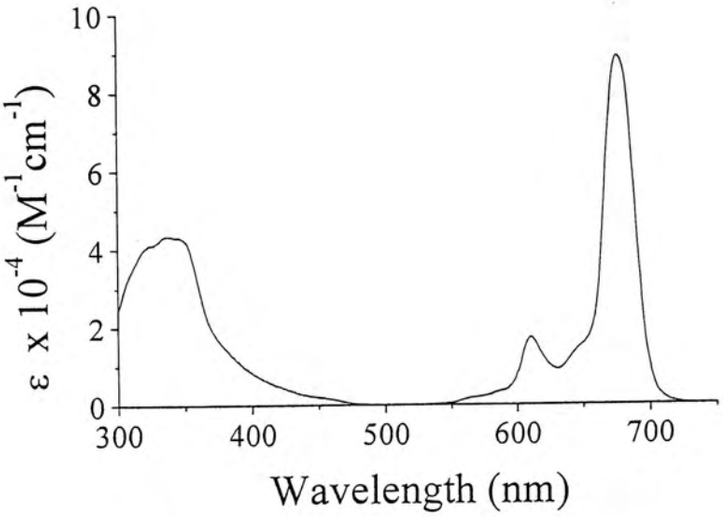
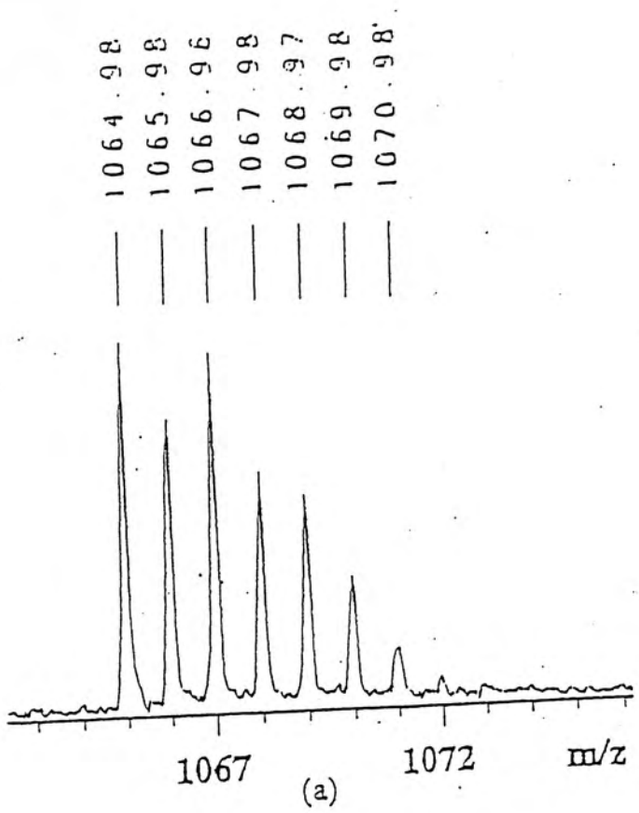
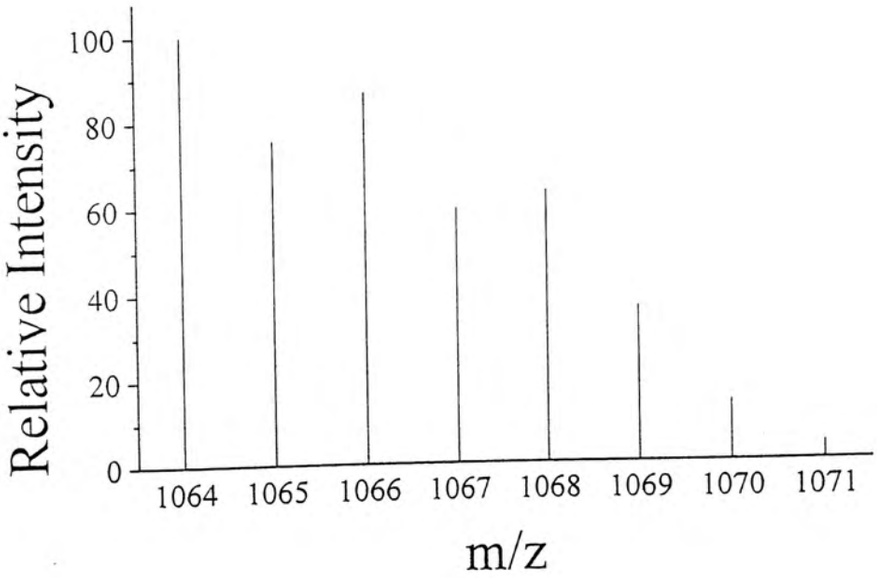


Figure 7. UV-Vis spectrum of **25** in THF.

Figure 8a shows the isotopic distribution of the molecular ion of **25**, which was observed in the MALDI-TOF mass spectrum. It can be seen that the pattern is closely related to the simulated spectrum as shown in Figure 8b.





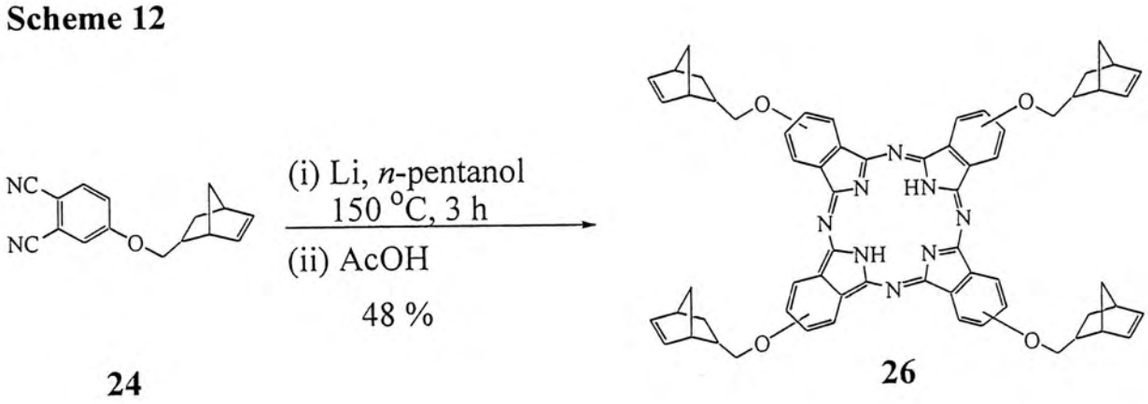
(b)

Figure 8. (a) Experimental and (b) simulated isotopic distribution of the molecular ion of **25**.

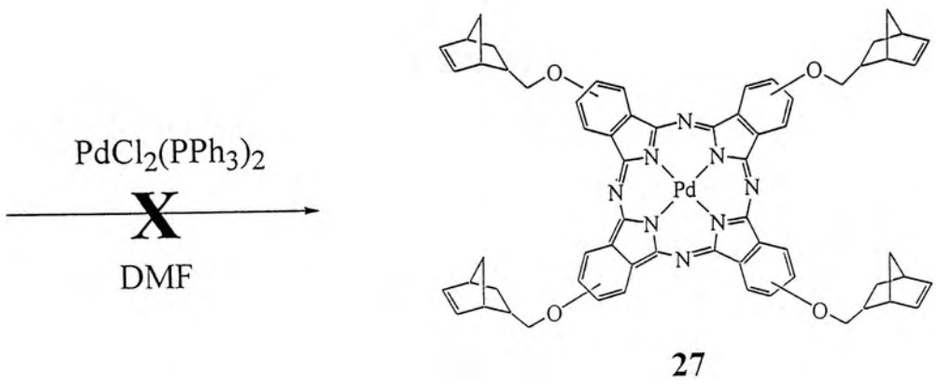
To study the metal effects on the properties of the resulting phthalocyanine-containing polymers, the palladium phthalocyanine analogue **27** was also prepared. Similar to the zinc(II) metal center, palladium(II) is also a closed shell metal ion. This heavy metal center, however, should have profound effects on the photophysical properties of the resulting polymers.

An initial attempt to prepare the palladium phthalocyanine **27** involved the metallation of the metal-free phthalocyanine **26** with a palladium(II) salt.[31] The metal-free phthalocyanine **26** was synthesized by cyclization of **24** with lithium in *n*-pentanol followed by acidic treatment (Scheme 12). The UV-Vis spectrum of this compound (Figure 9) showed a split Q band which is typical of metal-free phthalocyanines as a result of lowering in symmetry from D_{4h} to D_{2h} in the core. Treatment of **26** with a large excess of $PdCl_2(PPh_3)_2$ in DMF, however, only led to partial metallation. As shown by UV-Vis spectroscopy, a significant amount of unreacted metal-free phthalocyanine was still present, showing that this pathway is not suitable for the synthesis of the palladium phthalocyanine **27**.

Scheme 12



24 **26**



27

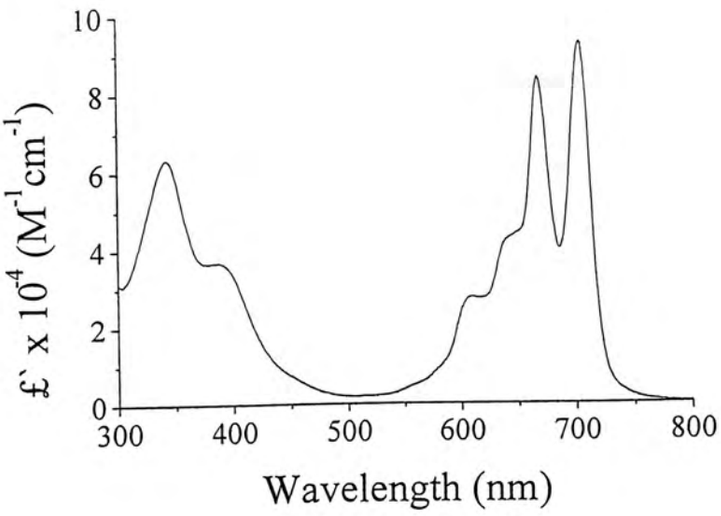
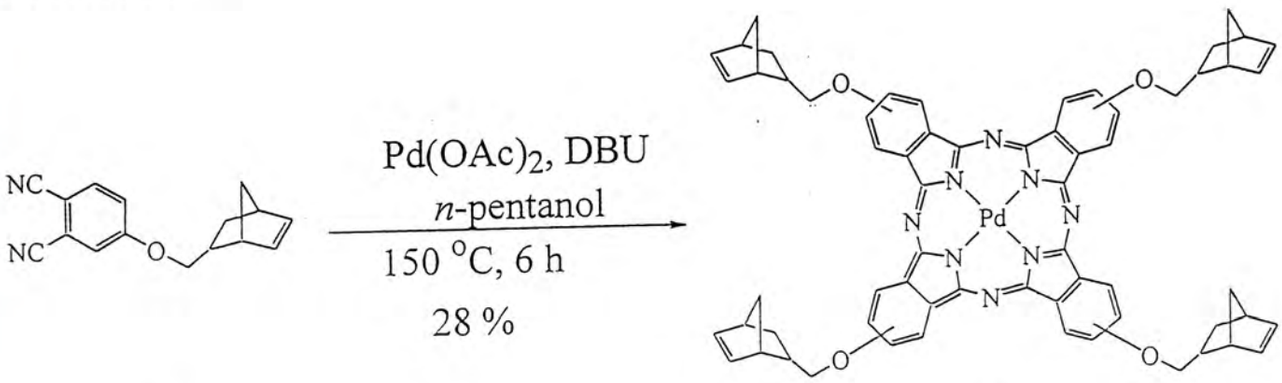


Figure 9. UV-Vis spectrum of **26** in THF.

The palladium phthalocyanine could however be synthesized with the method similar to that for **25**. Thus treatment of **24** with $Pd(OAc)_2$ and DBU in *n*-pentanol afforded the palladium phthalocyanine **27** (Scheme 13), which was purified by column chromatography followed by repeated precipitation. The solubility of this macrocycle in common organic solvents was significantly lower than that of the zinc(II) analogue.

Scheme 13



24 **27**

The UV-Vis spectrum of **27** is shown in Figure 10, which is quite different from that of **25** (Figure 7). The absorption at *ca.* 600 nm is relatively intense. To examine whether it is due to the aggregation effect, UV-Vis spectra of **27** in different concentrations were recorded. As shown in Figure 11, the ratio of the intensities of two bands increases from 1.63 to 3.00 in all the concentrations, showing that aggregation is significant for this compound in this concentration range.

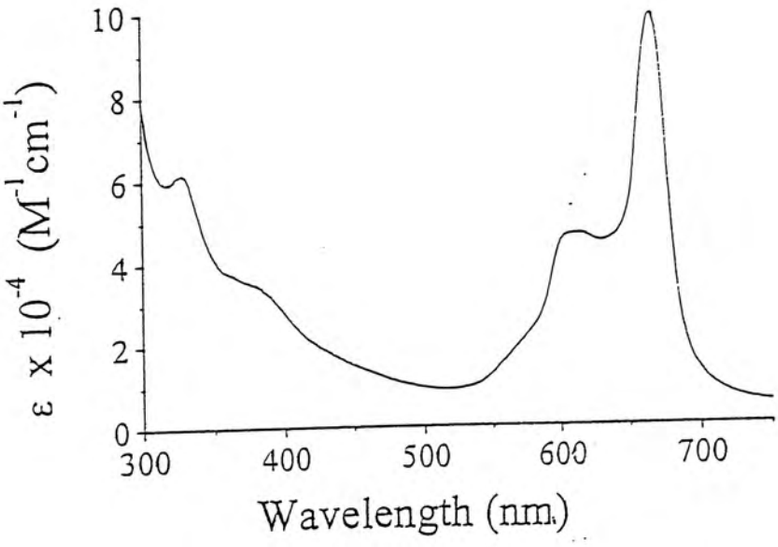


Figure 10. UV-Vis spectrum of 27 in THF.

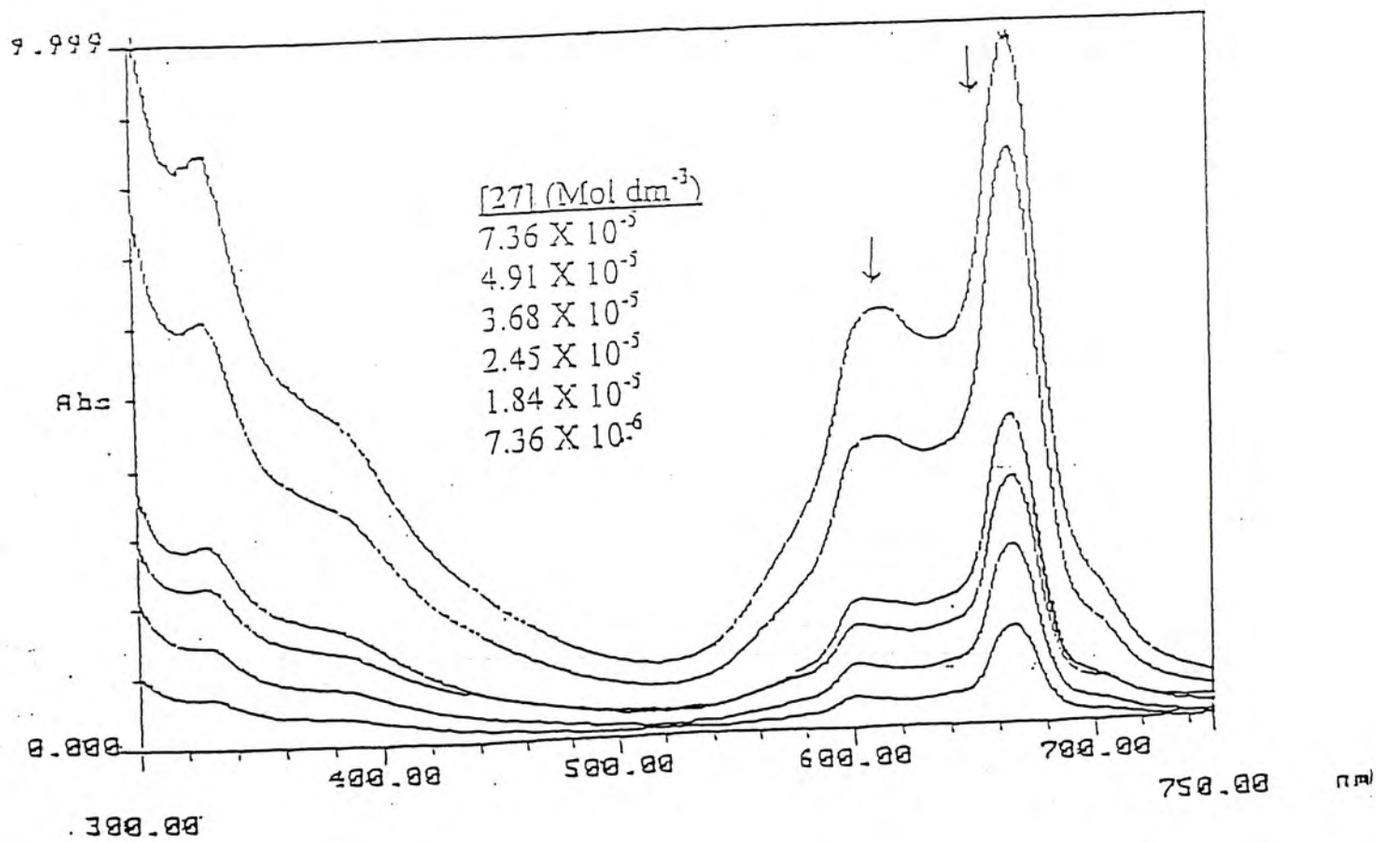
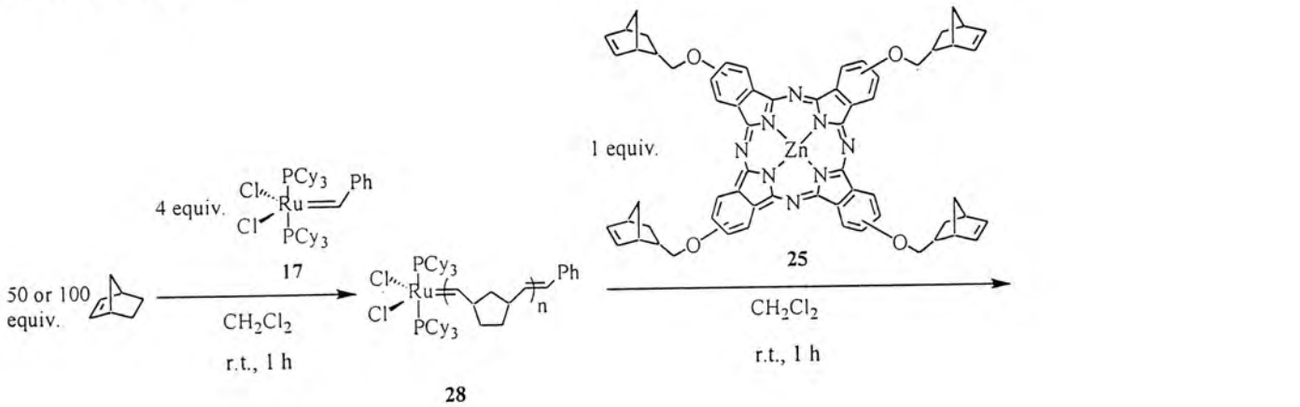


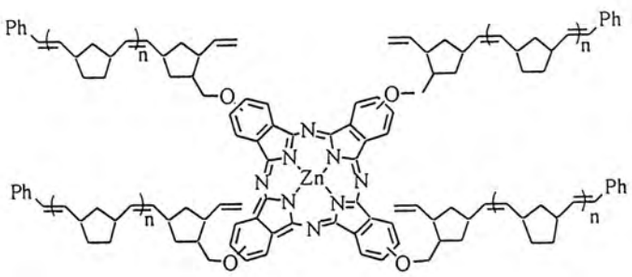
Figure 11. Variation of UV-Vis spectrum of 27 in THF with concentration.

2.1.2 *Polymerization of Tetra(norbornene) Phthalocyanines*

The norbornene substituents of the phthalocyanines can undergo a ring opening metathesis polymerization. Treatment of **25** with the Grubb's ruthenium catalyst **17** in CH_2Cl_2 led to the formation of a gel-like material immediately which had a very low solubility in organic solvents, probably due to an extensive cross linking process. To enhance the solubility of the resulting polymers, norbornene was first polymerized in CH_2Cl_2 using **17**, then phthalocyanine **25** was added (Scheme 14). This strategy will greatly reduce the extent of cross linking and enhance the solubility by incorporating long poly(norbornene) substituents to the phthalocyanine core.

Scheme 14





29 n ≈ 12.5 (71 %)

30 n ≈ 25 (69 %)

As shown in Scheme 14, 50 or 100 equiv. of norbornene (with respect to **25**) was treated with 4 equiv. of the catalyst **17** in CH_2Cl_2 at room temperature under nitrogen. During the course of the reaction, the color of the reaction mixture turned red and the viscosity increased steadily. By adding a small portion of the mixture into methanol, a white fibrous material was precipitated showing that a polymer was formed. A CH_2Cl_2 solution of **25** was then added to the reaction mixture, of which the color changed to deep green. To prevent the cross-linking process, a very diluted solution of **25** (10^{-5} M) was used which was added in a dropwise manner. After stirring for 1 h, the reaction mixture was exposed to air for 15 min, then added slowly to methanol to give a green fibrous material which was collected by filtration. UV-Vis spectrum of the pale green filtrate did not show absorptions in the Q band region, indicating that all phthalocyanine had been incorporated into the polymer.

Figures 12 and 13 show the UV-Vis spectra of the polymers **29** and **30** in THF. Both of them resemble each other and display typical absorptions of slightly aggregated metallophthalocyanines. The rather intense broad band at *ca.* 610 nm can be attributed to the aggregated species.[32] The different length of the polymeric substituents does not cause significant influence on the absorption spectra.

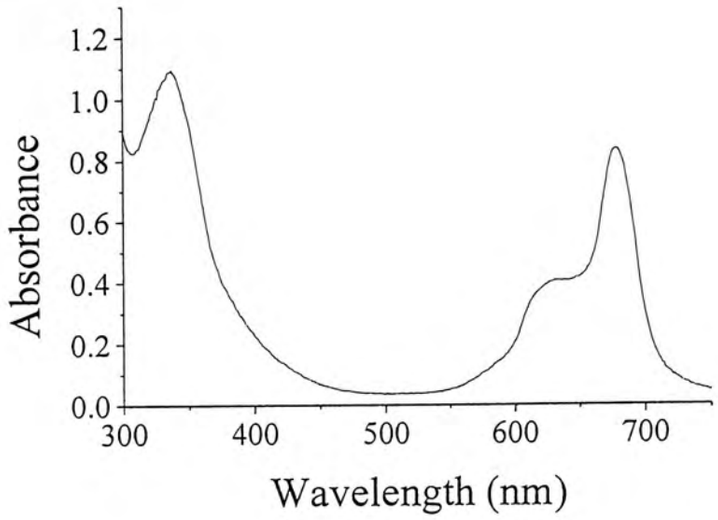


Figure 12. UV-Vis spectrum of **29** in THF; [**29**]: 3.5 mg in 10 cm^3 THF.

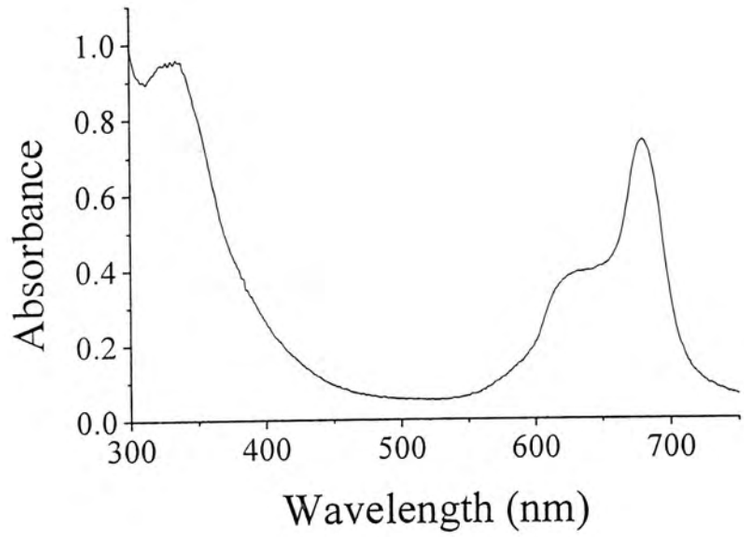
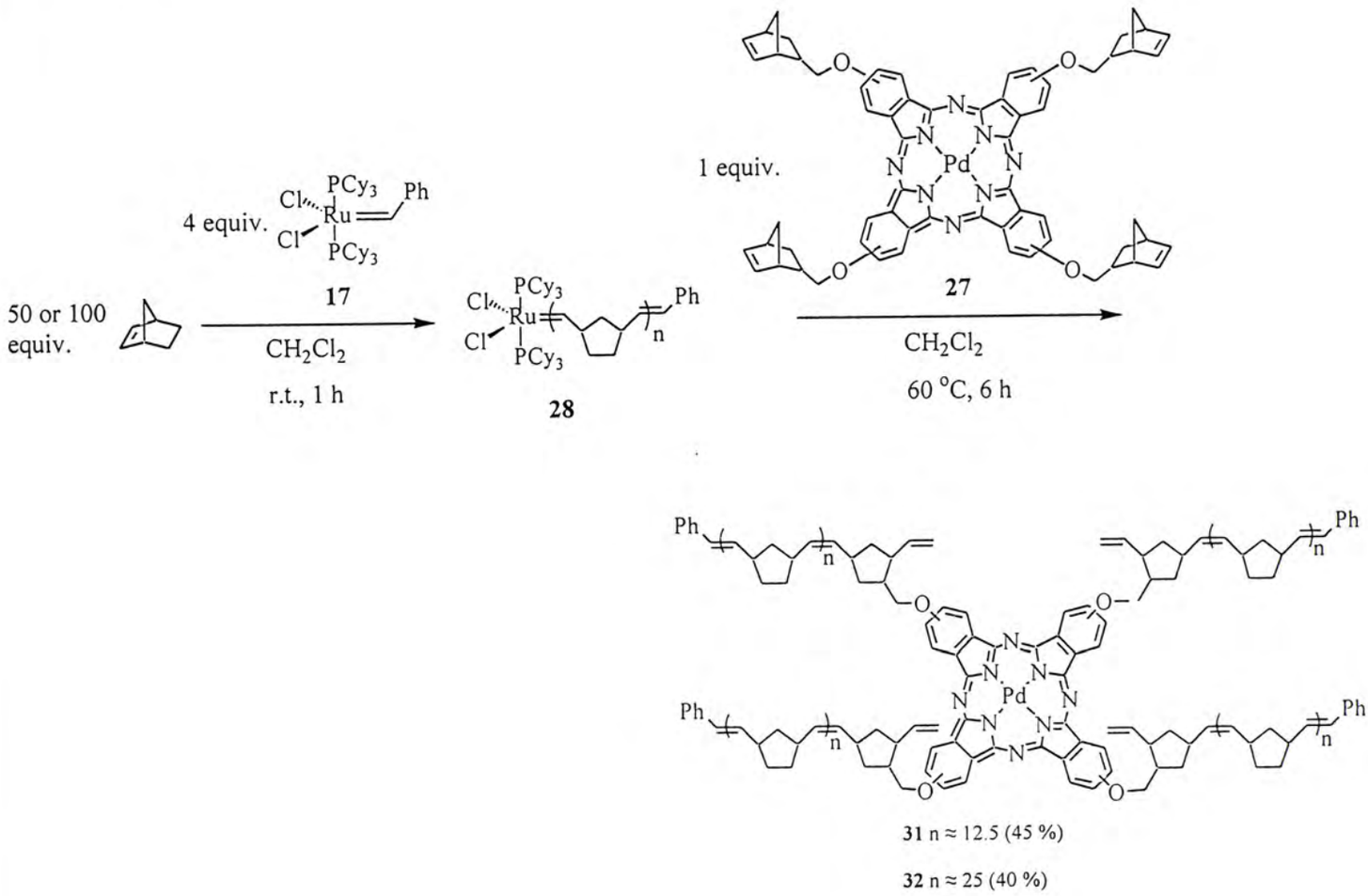


Figure 13. UV-Vis spectrum of **30** in THF; [**30**]: 3.2 mg in 10 cm^3 THF.

The palladium phthalocyanine **27** was also co-polymerized with norbornene in a similar manner (Scheme 15). However, due to the lower solubility of **27** compared with **25**, a higher temperature and a longer reaction time were required. The palladium phthalocyanine

containing polymers **31** and **32** were isolated in 40 – 45 % yield, whose color was deeper than that of the zinc phthalocyanine analogues.

Scheme 15



The UV-Vis spectra of **31** and **32** are given in Figures 14 and 15. Both spectra show two absorptions in the Q band region. The band at *ca.* 610 nm, which can be attributed to the aggregated species is more intense than the monomeric Q band, showing that the aggregation tendency of these polymeric phthalocyanines is higher than that of the zinc analogues.

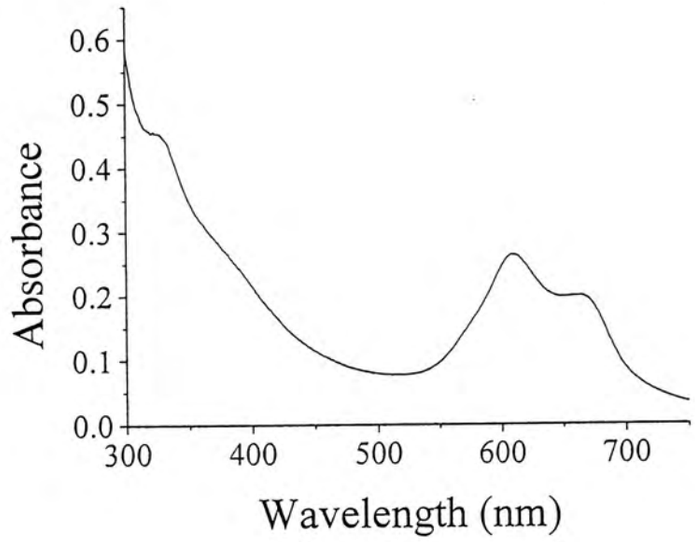


Figure 14. UV-Vis spectrum of **31** in THF; [**31**]: 2.7 mg in 10 cm^3 THF.

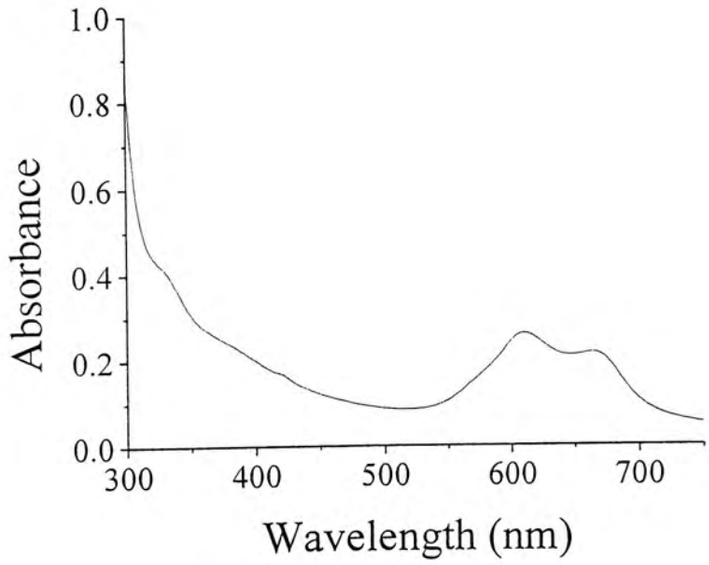
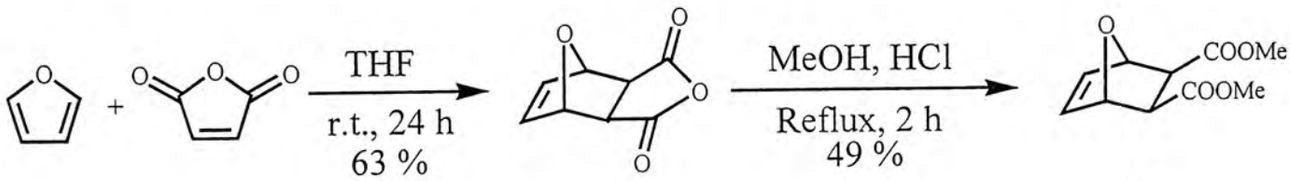


Figure 15. UV-Vis spectrum of **32** in THF; [**32**]: 2.5 mg in 10 cm^3 THF.

To enhance the solubilities of the resulting polymers and examine the effects of polymer backbone on the spectral and photophysical properties of the phthalocyanine core, monomer **34**

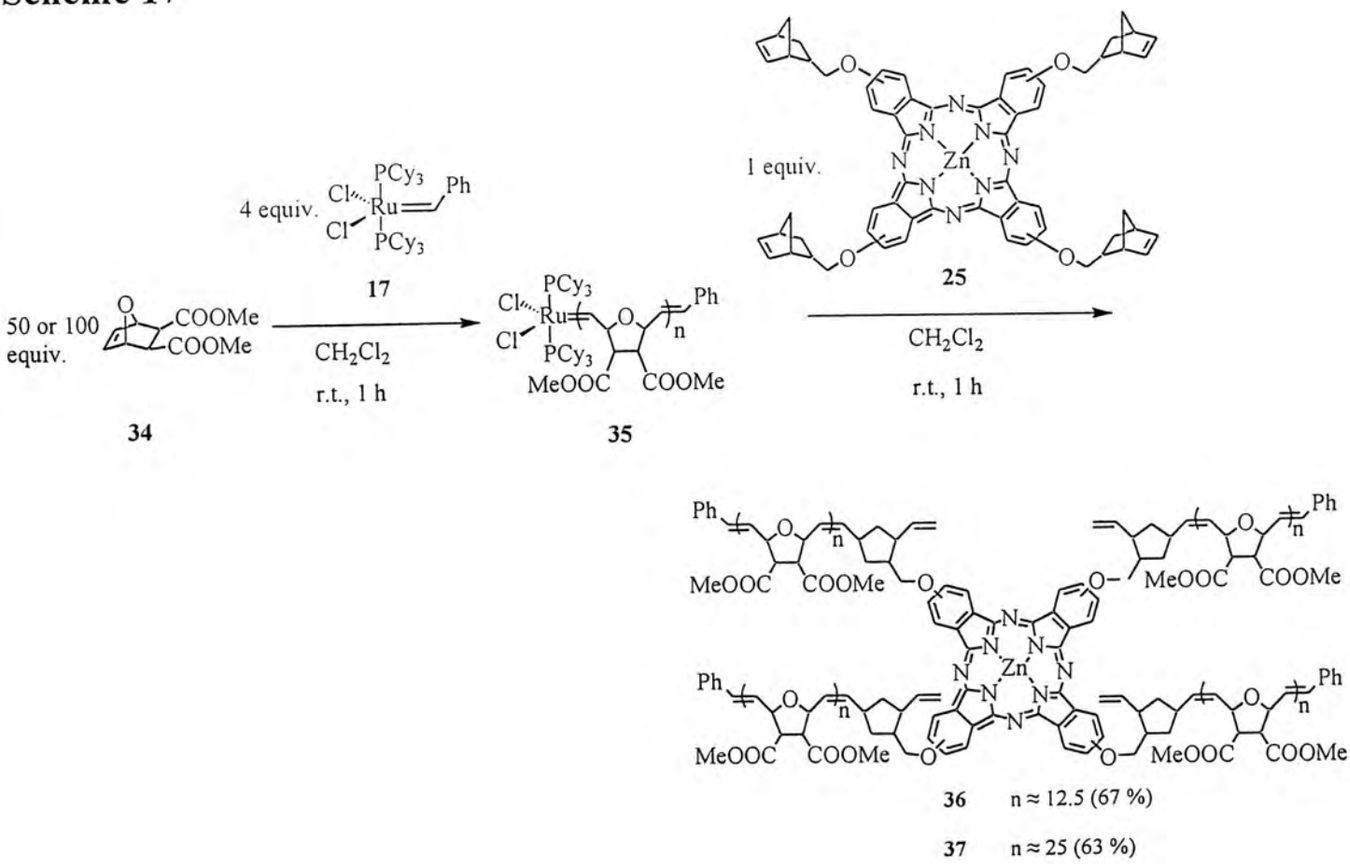
was prepared according to the route shown in Scheme 16. Diel-Alder reaction of furan and maleic anhydride in THF at room temperature gave the adduct **33**, which upon treatment with methanol and hydrochloric acid led to the formation of **34**.[33] This 7-oxanorbornene derivative was then polymerized using the method described in Scheme 14,[34] giving polymers **36** and **37** as a green solid (Scheme 17).

Scheme 16



33 **34**

Scheme 17



34 **35**

36 n ≈ 12.5 (67 %)

37 n ≈ 25 (63 %)

The solubility of these polymers is significantly higher than that of **29** and **30**, which do not contain the ester functionalities. They are readily soluble in THF without heating and are also soluble in chloroform and dichloromethane.

The UV-Vis spectra of **36** and **37** show a relatively sharp Q band at 680 nm (Figure 16 and 17). These results suggest that the aggregation tendency of these polymers is significantly lower than that of the unsubstituted poly(norbornene)s **29** and **30**.

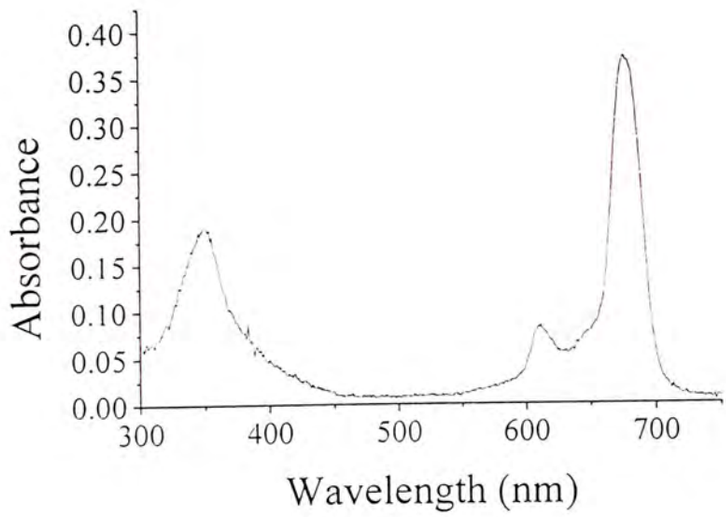


Figure 16. UV-Vis spectrum of **36** in THF; [**36**]: 3.0 mg in 10 cm^3 THF.

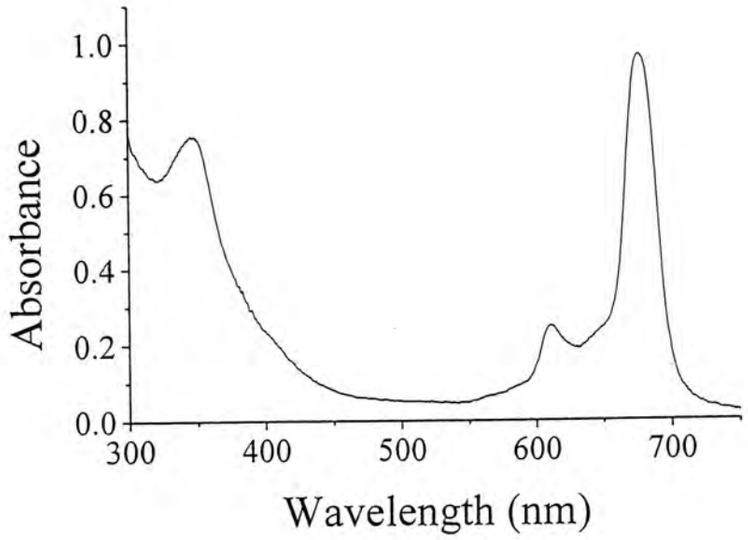
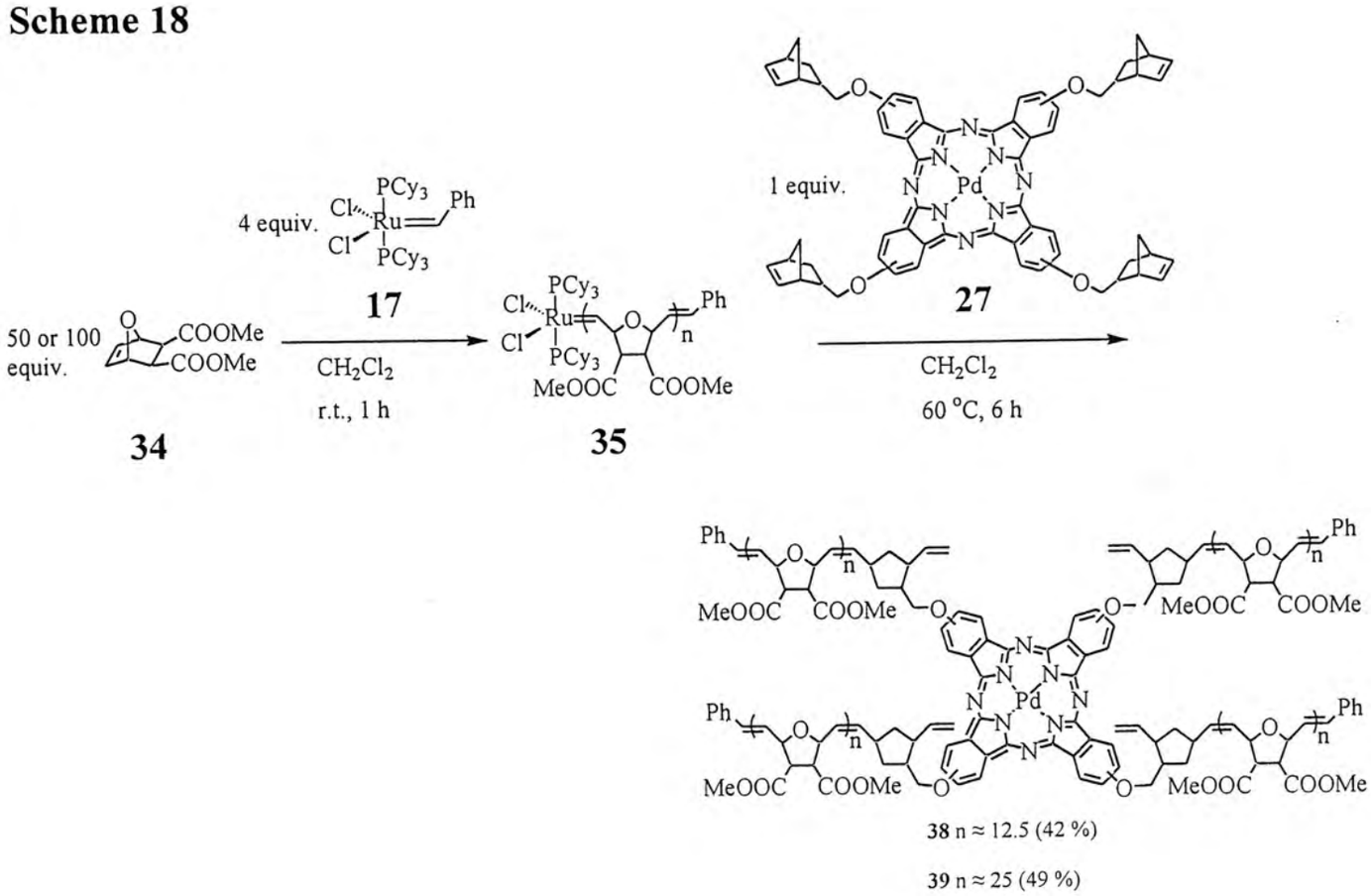


Figure 17. UV-Vis spectrum of **37** in THF; [**37**]: 3.0 mg in 10 cm^3 THF.

The palladium analogues **38** and **39** were prepared similarly using palladium phthalocyanine **27** except that a higher temperature and a longer reaction time were required for the polymerization. The solubility of these polymers was better than that of the unsubstituted poly(norbornene)s **31** and **32**. As shown in Figures 18 and 19, the UV-Vis spectra of these two polymers are similar to those of **31** and **32**, showing that aggregation is still significant in these two polymers.

Scheme 18



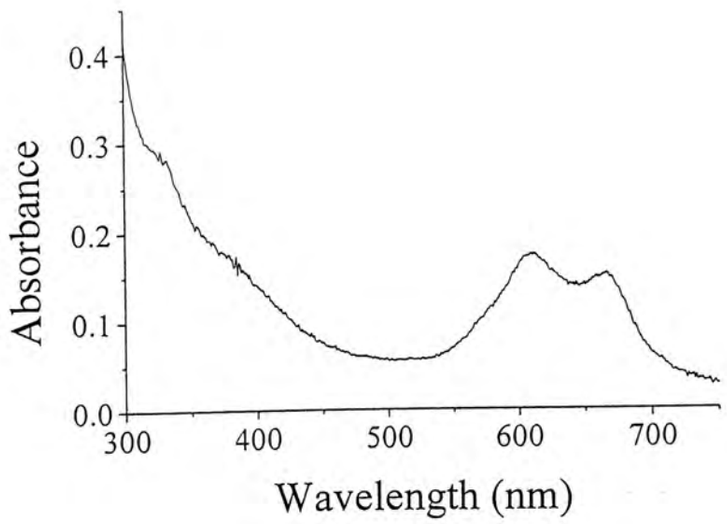


Figure 18. UV-Vis spectrum of **38** in THF; [**38**]: 2.6 mg in 10 cm^3 THF.

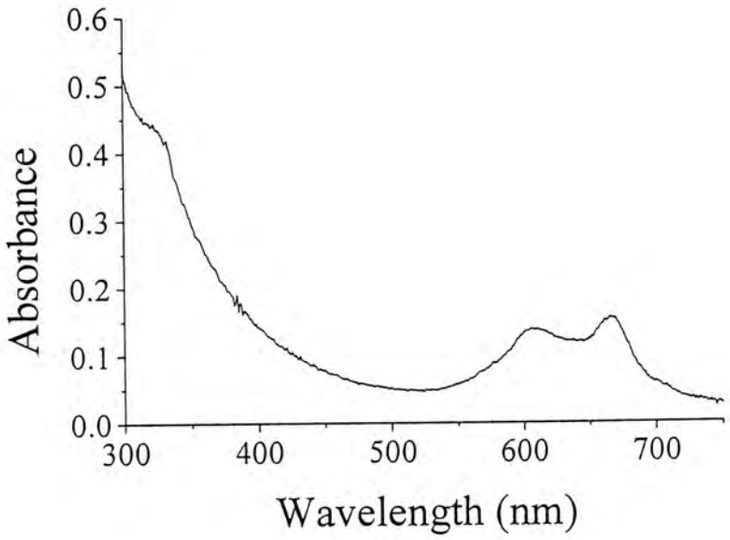


Figure 19. UV-Vis spectrum of **39** in THF; [**39**]: 2.5 mg in 10 cm^3 THF.

2.1.3 Characterization of the Polymers

The phthalocyanine-containing polymers were characterized with NMR spectroscopy. All the poly(norbornene)s gave very similar ^1H and $^{13}C\{^1H\}$ NMR spectra. Figure 20 shows the ^1H NMR spectrum of **31** for exemplification. The signals at *ca.* δ 5.4 and 5.2 can be assigned to the *trans* and *cis* olefinic protons, respectively in *ca.* 6.3 : 1 ratio.[35] The presence of *cis* and *trans* double bonds in the polymer backbone was also confirmed by $^{13}C\{^1H\}$ NMR spectroscopy. Figure 21 shows the $^{13}C\{^1H\}$ NMR spectrum of **29** with assignment according to literature data.[36] It is clear that *trans* double bonds are dominant in this polymer.

All the poly(7-oxanorbornene)s also gave similar NMR spectra. Figures 22 and 23 show the ^1H and ^{13}C NMR spectra of **37** and **38** respectively, which are typical. It can be seen in Figure 22 that the signals at δ 5.60 and 5.58 represent the *cis* and *trans* olefinic protons (in *ca.*

1.2: 1).[37] The olefinic carbons' signals appear at *ca.* δ 130 having a similar relative intensity.

It is worth noting that the aromatic signals for the phthalocyanine ring were not observed in the ^{1}H and ^{13}C NMR spectra. It may be due to the fact that the phthalocyanine portion is small in the polymers. Moreover the substituted phthalocyanine core exists as a mixture of constitutional isomers which makes the ring protons inequivalent. The observation can also be explained by the aggregation phenomenon which will significantly broaden the signals.[38]

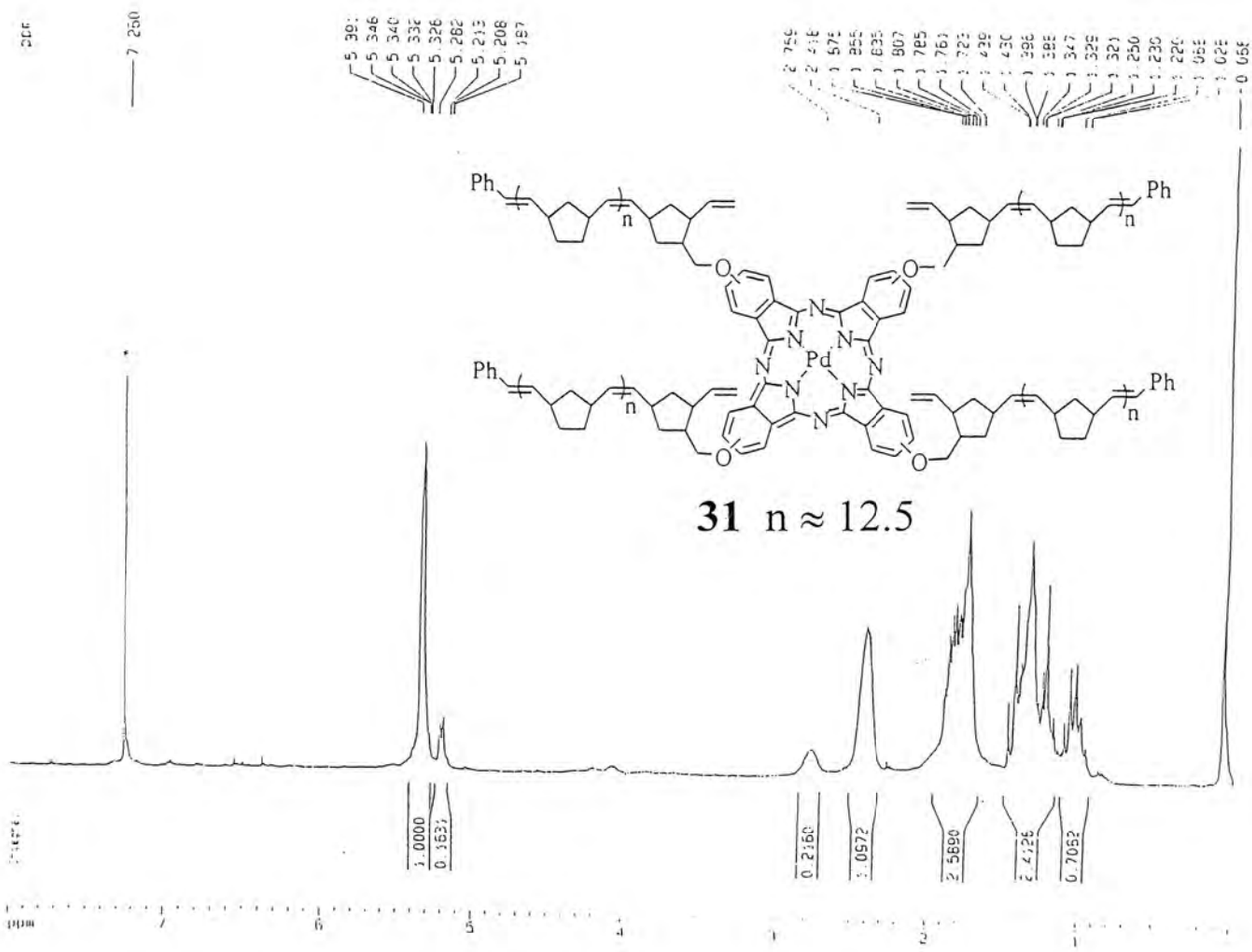


Figure 20. ^{1}H NMR spectrum of **31** in $CDCl_3$; * indicates the solvent peak.

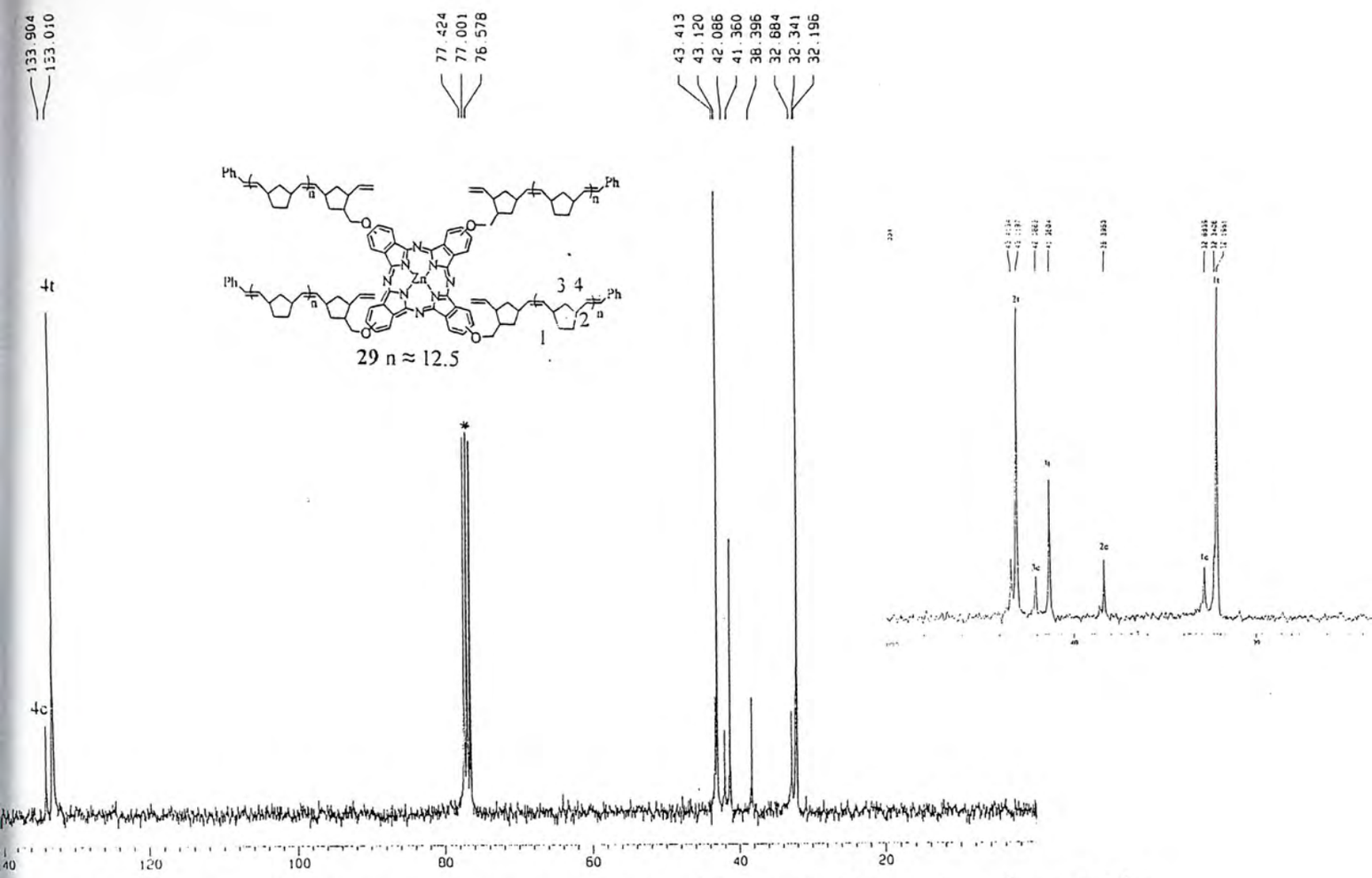


Figure 21. $^{13}C\{^{1}H\}$NMR spectrum of **29** in $CDCl_3$; * indicates the solvent peaks.

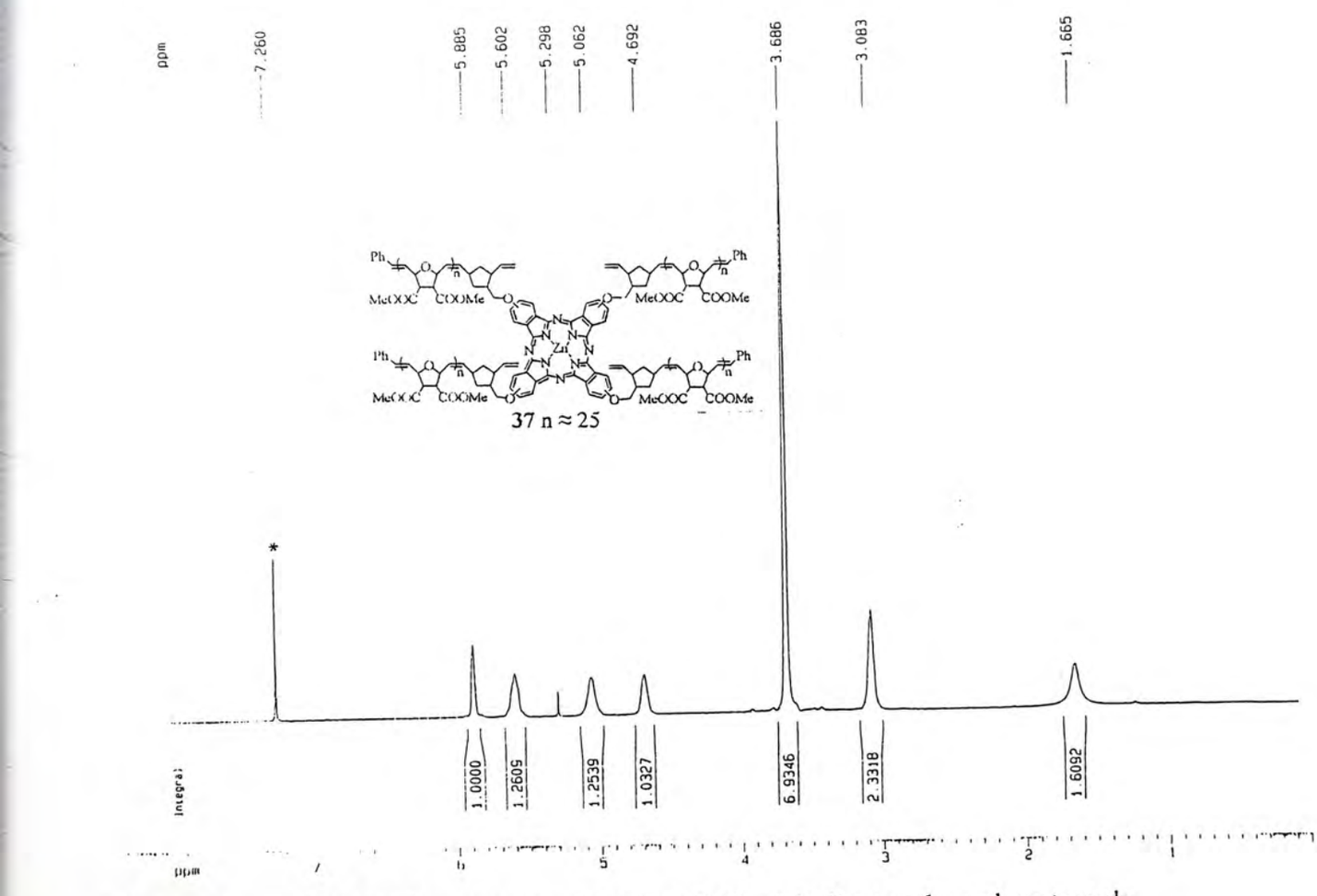


Figure 22. ^{1}H NMR spectrum of **37** in $CDCl_3$; * indicates the solvent peak.

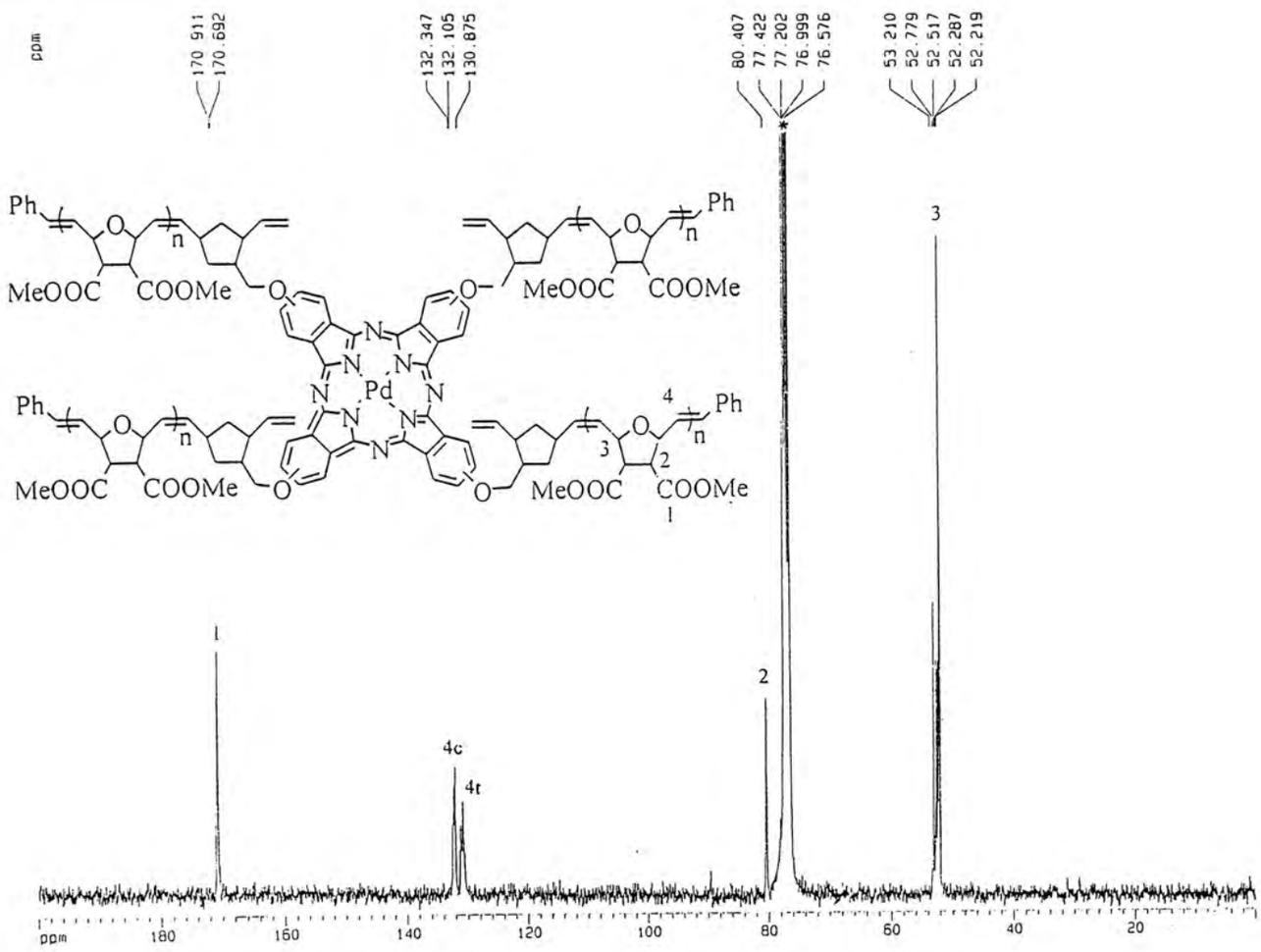


Figure 23. $^{13}C\{^{1}H\}$NMR spectrum of **38** in $CDCl_3$; * indicates the solvent peaks.

The molecular weight and polydispersity of all the phthalocyanine-containing polymers were determined by GPC in THF using polystyrene as the standard. The data together with the glass transition temperature (T_g) are given in Table 1. It has been found that by using **17** as the catalyst the polydispersity index (PDI) of the homopolymer of norbornene is 1.10,[27] while that of the poly(7-oxanorbornene) with 2,3-methoxycarbonyl substituents is 1.13.[39] The PDI of poly(norbornene)s with other substituents could be as high as 2.11,[40, 41] showing that the PDI of polymers prepared by **17** is sensitive to the substituents on the norbornene-type monomers. The PDI values of these polymers, in particular the poly(norbornene)s **29** and **30**, are significantly

larger than those of poly(norbornene) and poly(7-oxanorbornene) without the phthalocyanine moieties. This can be attributed to the cross linkage process between the polymer chains.

The typical T_g value of poly(norbornene) is around 35 °C.[42] The higher T_g values of polymers **29** and **30** can also be attributed to the cross-linkage processes. The T_g value of the poly(7-oxanorbornene) is about 70 °C according to the literature.[43] The data for **36** and **37** were close to that value, which may indicate that cross-linking in this polymer system was less significant than that in the poly(norbornene).

Polymer	T_g (°C)	M_n	Polydispersity (PDI)
29	84	49,900	2.93
30	84	78,400	2.27
31	Not completely soluble		
32	Not completely soluble		
36	73	37,900	1.51
37	77	111,200	1.44
38	-	58,600	1.56
39	-	159,800	1.20

Table 1. GPC analysis (in THF) and thermal properties of polymers **29 –32** and **36 - 39**.

2.1.4 Photophysical Properties of the Polymers

The UV-Vis spectra of the polymers **29 – 32** and **36 – 39** are shown and discussed in the

previous section. This section reports the photophysical properties of these polymers as probed by steady-state and transient spectroscopy. The data for the phthalocyanine monomers **25** and **27** are also included for comparison.

All the phthalocyanine monomers **25** and **27** and the polymers **29 – 32** and **36 – 39** showed a fluorescence emission at *ca.* 680 nm upon excitation at 610 nm. The fluorescence quantum yields were determined using unsubstituted zinc(II) phthalocyanine as the reference (Φ = 0.30 in 1-chloronaphthalene).[44] The concentration of **25** and **27** were 1.76 X 10^{-6} Mol dm^{-3} and 1.25 X 10^{-6} Mol dm^{-3} respectively and the polymers were *ca.* 1.0 mg in 10 cm^3. The data are compiled in Table 2.

	Quantum yield
ZnPc **25**	0.29
29	0.03
30	0.01
36	0.29
37	0.21
PdPc **27**	0.12
31	0.03
32	0.03
38	0.17
39	0.15

Table 2. Fluorescence quantum yields of the phthalocyanine monomers **25** and **27**, and the polymers in THF

For the zinc phthalocyanine monomer **25**, the quantum yield is 0.29, which is almost the same as that of the unsubstituted zinc phthalocyanine. The value of the palladium analogue **27**

is significantly lower. It could be due to the higher aggregation tendency as shown by UV-Vis spectroscopy which enhances the internal conversion. The heavy atom effect may also play a role which promotes the intersystem crossing process.[45]

The quantum yields of polymeric zinc phthalocyanines **29**, **30**, **36**, and **37** are different depending on the polymer backbone. The UV-Vis spectra of **29** and **30** (p. 32) suggest that there is significant aggregation of the phthalocyanine units which will reduce the fluorescence quantum yield.[46] The results are consistent with the UV-Vis spectroscopic studies of **36** and **37** (Figures 16 and 17), which reveal that the phthalocyanine core is relatively free from aggregation in these polymer systems.

Similar results were obtained for the palladium phthalocyanine polymers. The quantum yields for poly(norbornene)s **31** and **32** are very low due to the higher aggregation tendency in THF. The fluorescence quantum yield values for the poly(7-oxanorbornene) derivatives **38** and **39** are significantly higher because of the less aggregation. The values, however, are still lower than those of the zinc analogues **36** and **37**, which are relatively free from molecular aggregation. Again, the heavy atom effect due to the palladium(II) center may also be one of the factors reducing the fluorescence quantum yield.

The fluorescence lifetime (τ_{s1}), repopulating time of the ground state (τ_{s0}), and the quantum yield of intersystem crossing (Φ_{ISC}) were also determined by time correlated single photon counting (TCSPC) technique and transient absorption spectroscopy (TAS), respectively.

The data for the zinc phthalocyanine monomer **25** and polymers **29**, **30**, **36** and **37** are compiled in Table 3. It can be seen that τ_{s1} of the monomer **25** is slightly longer than those of the polymers. It is likely that the competing internal conversion process is facilitated by the aggregation of phthalocyanine and the polymer backbones themselves, giving a shorter fluorescence lifetime for the polymers.

	TCSPC	TAS	
	τ_{s1} (ns) $\pm$ 0.1 ns	τ_{s0} (ns)	Φ_{ISC}
ZnPc **25**	3.2	2.4	65 %
29	2.5	1.6	26 %
30	2.8	1.0	< 20 %
36	2.3	1.6	23 %
37	3.1	4.3	53 %

Table 3. Photophysical properties of the zinc phthalocyanine monomer **25** and the polymers **29**, **30**, **36**, and **37**.

The repopulation of the ground state was shown in the introduction which includes three major pathways, namely the radiative fluorescence emission, non-radiative internal conversion from the first excited singlet state to the ground state and the radiative phosphorescence emission from the first excited triplet state to the ground state. As a result, τ_{s0}, the repopulation

time of the ground time, should always be smaller than τ_{s1} as shown in Table 3. The longer τ_{s0} for **37** suggests that the sample may contain a trace amount of impurities.

Φ_{ISC} is the quantum yield of intersystem crossing, which competes with the fluorescence emission and the internal conversion processes. Since the phthalocyanine core tends to be more aggregated in polymeric environment and aggregation of phthalocyanine will normally increase the rate of internal conversion, it is not unexpected that the value of Φ_{ISC} is smaller for polymeric systems (Table 3).[47]

Table 4 shows the corresponding data for the palladium analogues. The τ_s of **27** (5.3 ns) is longer than the typical values for palladium phthalocyanines. It is likely that the sample contains trace amount of impurities, most probably the metal-free phthalocyanine. To prove this proposition, the excitation spectrum of **27** was measured which was found to be different from the absorption spectrum. Fluorescence spectroscopy is much more sensitive than absorption spectroscopy and the UV-Vis spectrum of **27** does not show the features of metal-free phthalocyanines. Thus impurities should only be present in very small quantity.

The repopulation times of the ground state of the polymers were found to be ca. 100 ps. Since such values are typical for rotational decay times, we measured the transient spectra parallel and perpendicular to the polarization of the exciting laser pulse. It can be seen in Table 4, that the orientation of observation has no influence on the τ_{s0} and Φ_{ISC} values. It can be concluded that the measured values are the real times of repopulation of the ground state of the

palladium phthalocyanines and not the rotational diffusion times.

The Φ_{ISC} values of these polymers are consistently higher than those of the zinc analogues (Table 3). This can be attributed to the heavy atom effect which promotes the intersystem crossing process.

	TCSPC	TAS	
	τ_{s1} (ns) ±0.1 ns	τ_{s0} (ns)	Φ_{ISC}
PdPc **27**	5.3	4	96 %
31 //		0.15	57 %
31 ⊥		0.1	60 %
32 //		0.18	45 %
32 ⊥		0.1	47 %
38 //		0.09	45 %
38 ⊥		0.1	50 %
39 //		0.09	61 %
39 ⊥		0.08	61 %

Table 4. Photophysical properties of the palladium phthalocyanine monomer **27** and the polymers **31**, **32**, **38**, and **39**.

2.2 Phthalocyanines Substituted with One Poly(norbornene)

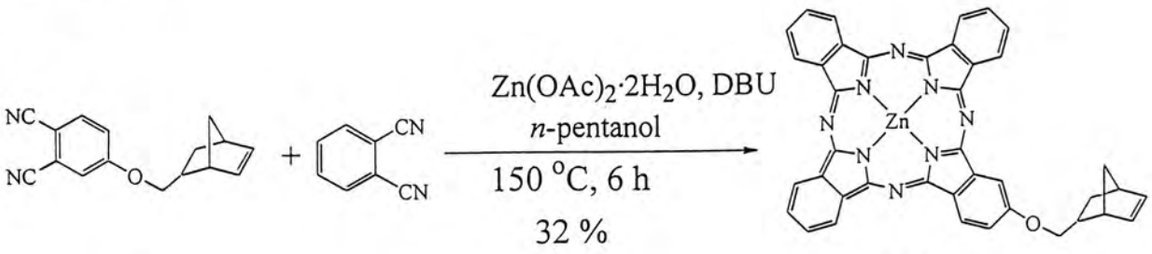
2.2.1 Preparation and Polymerization of Mono(norbornene) Phthalocyanine

As reported in the previous section, phthalocyanines substituted with four poly(norbornene) chains are usually aggregated and have low solubility. To circumvent these problems arising from the cross-linking process, the unsymmetrical phthalocyanine **40**, which contains only one norbornene substituent was synthesized by mixed cyclization.

Mixed condensation is one of the most commonly used methods to synthesize unsymmetrical phthalocyanines. It is convenient, but a mixture of differently substituted phthalocyanines is usually formed which are not easy to separate.[48]

By using twenty-fold excess of 1,2-dicyanobenzene to react with the norbornene-substituted phthalonitrile **24**, unsubstituted phthalocyanine together with the mono- and di-substituted phthalocyanines were formed. Due to the poor solubility of the former compound, it could not be eluted out during chromatography, while the latter two macrocycles could be readily separated by chromatography using ethyl acetate and *n*-hexane (2 : 1) as eluent. Under these conditions, the mono norbornene-substituted phthalocyanine **40** was obtained in 32 % yield (Scheme 19). The blue product could be further purified by re-precipitation using hexane and methanol.

Scheme 19



24 **40**

The UV-Vis spectrum of **40** in THF is shown in Figure 24. It is a typical spectrum for non-aggregated metallophthalocyanines, giving the λ_{max} at 341 (B band), 601 (vibronic band), and 665 nm(Q band).

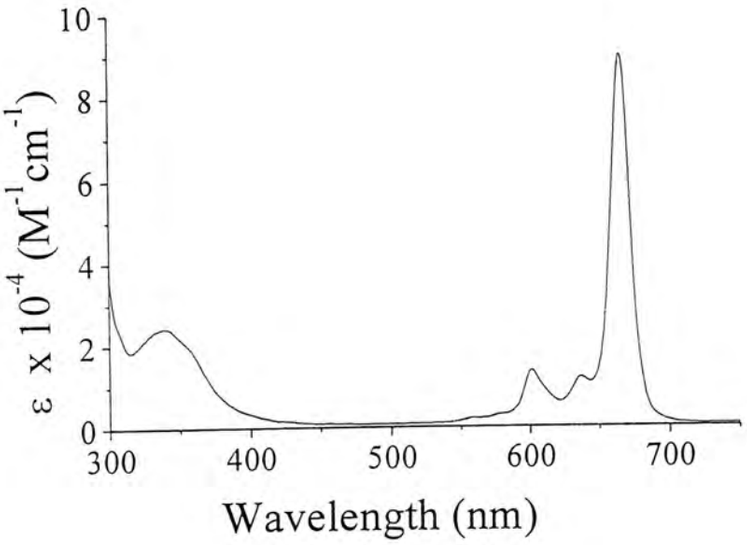
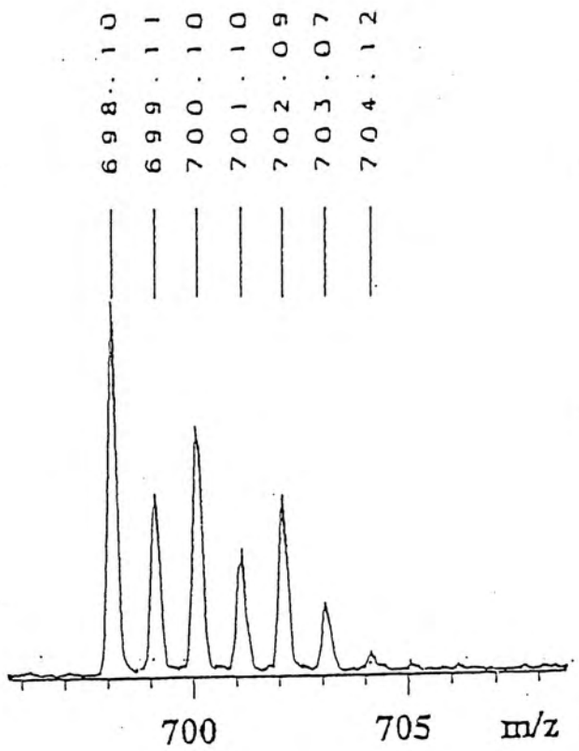
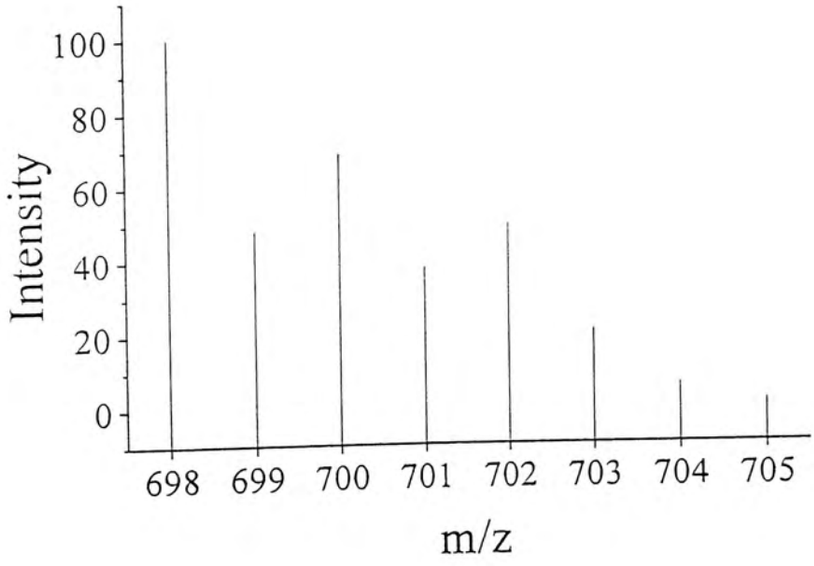


Figure 24. UV-Vis spectrum of **40** in THF.

Compound **40** was also characterized by MALDI-TOF mass spectroscopy. As shown in Figure 25, the experimental isotopic distribution for the molecular ion closely resembles the simulated pattern which provides as unambiguous characterization of the species.



(a)

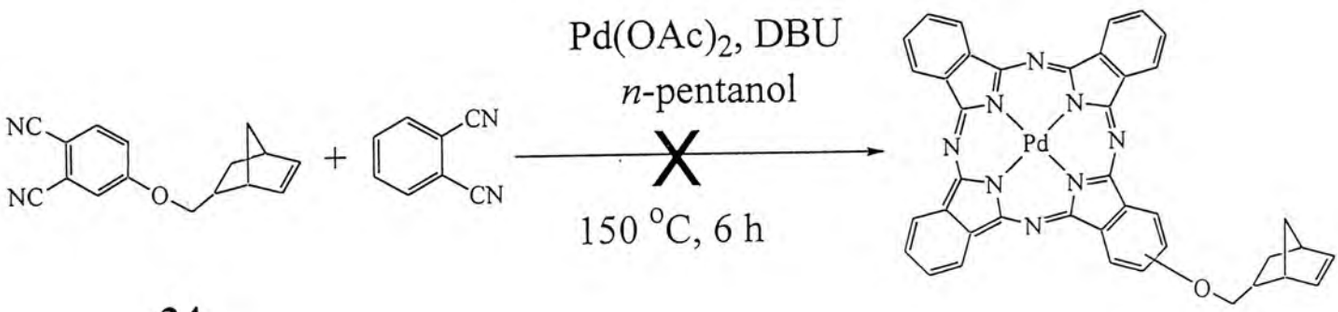


(b)

Figure 25. (a) Experimental and (b) simulated isotopic distribution of the molecular ion of **40**.

Attempts were also made to prepare the unsymmetrical palladium analogue using a similar procedure (Scheme 20). The color of the reaction mixture turned green during cyclization, but changed to red when it was subjected to column chromatography, showing that the palladium phthalocyanines are unstable and cannot be isolated readily.

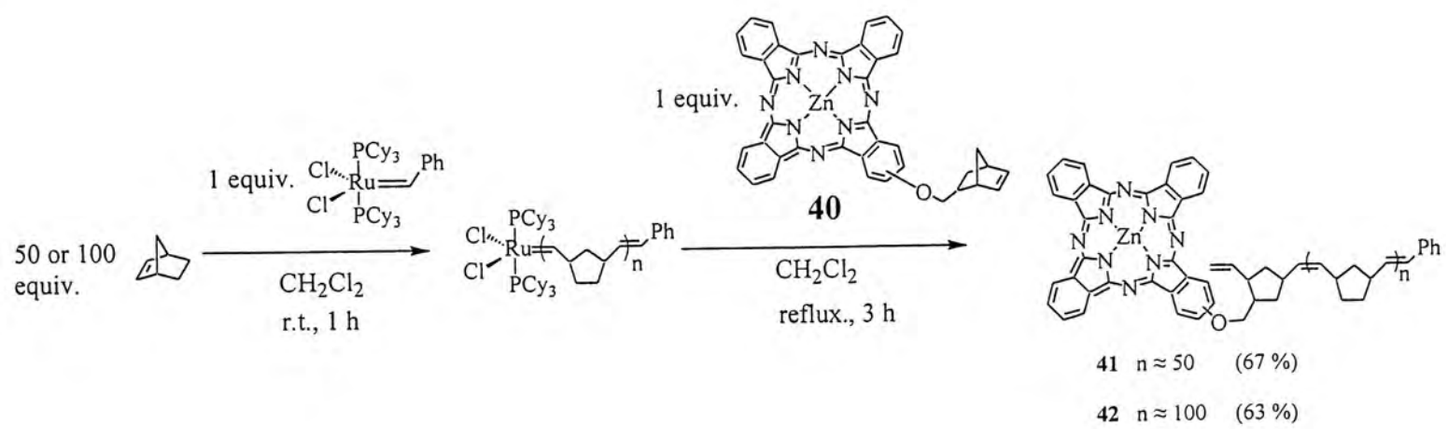
Scheme 20



24

Homopolymerization of the mono-substituted phthalocyanine **40** was attempted, but it appeared that no reaction occurred even under refluxing conditions for a few days. It is likely that the phthalocyanine ring is too bulky and hinders the polymerization process. This kind of polymerization, however, has been reported in which the phthalocyanine ring and the polymerizing group are separated by a long spacer.[22] The unsymmetrical macrocycle **40**, however, can be copolymerized with norbornene as shown in Scheme 21.

Scheme 21



41 n ≈ 50 (67 %)

42 n ≈ 100 (63 %)

The polymers are highly soluble in THF, showing that cross-linking is greatly reduced for this mono substituted system. As shown in Figures 26 and 27, the UV-Vis spectra of these two polymers in THF give a very sharp Q band, suggesting that the polymers are less aggregated than the polymers **29** and **30** prepared from the tetra-substituted phthalocyanine **25**. These results clearly show that the polymeric chain can enhance the solubility of the phthalocyanine core and reduce the aggregation tendency of the macrocycle.

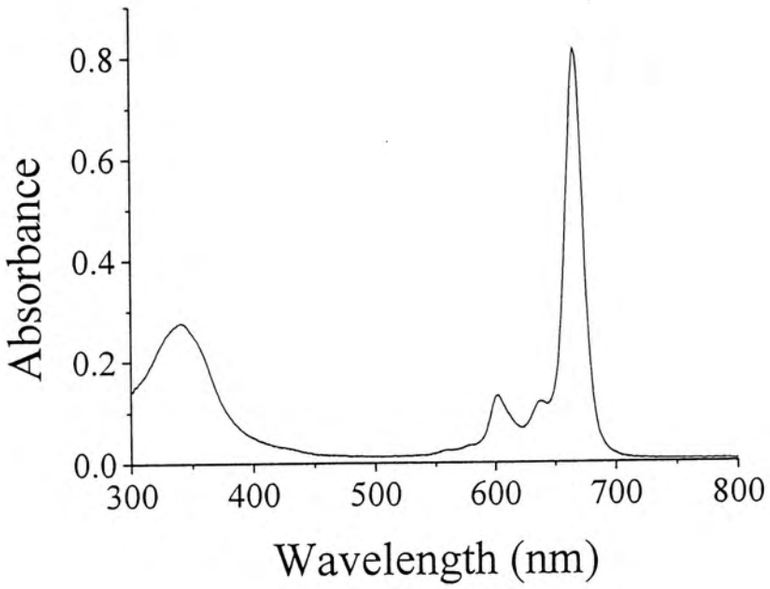


Figure 26. UV-Vis spectrum of **41** in THF; [**41**]: 3.0 mg in 10 cm^3 THF.

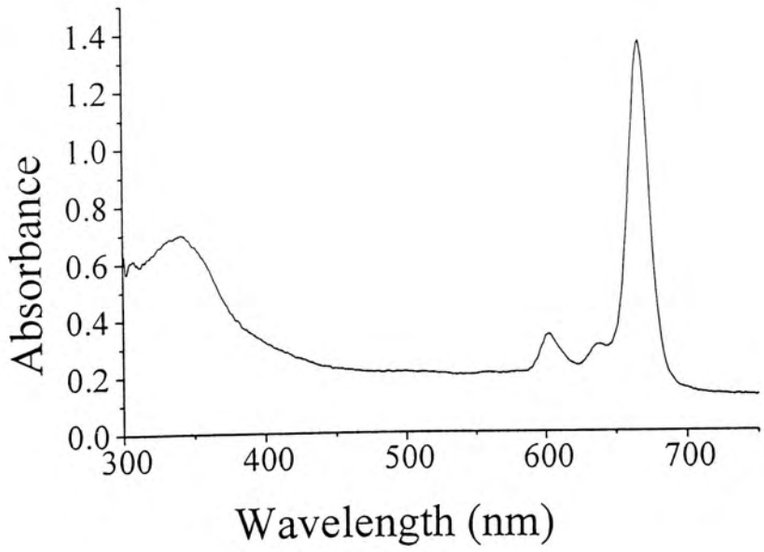
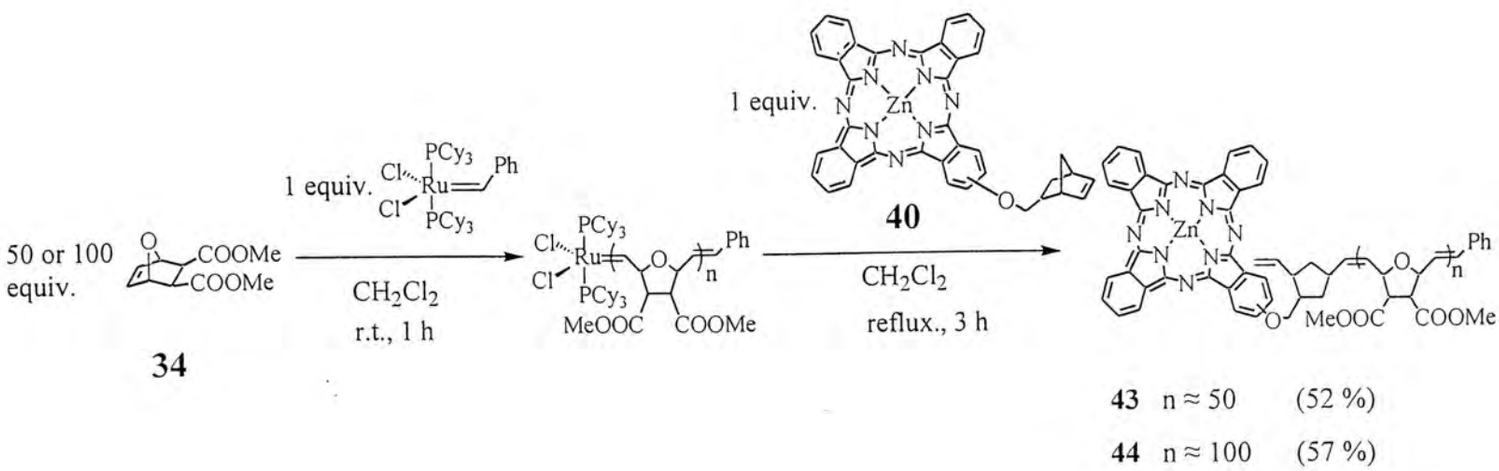


Figure 27. UV-Vis spectrum of **42** in THF; [**42**]: 3.5 mg in 10 cm^3 THF.

Scheme 22



43 n ≈ 50 (52 %)

44 n ≈ 100 (57 %)

By using a similar methodology, the poly(7-oxanorbornenes) **43** and **44** were prepared using **34** as the monomer. As expected, the resulting polymers are highly soluble in THF giving UV-Vis spectra typical of non-aggregated phthalocyanines (Figures 28 and 29).

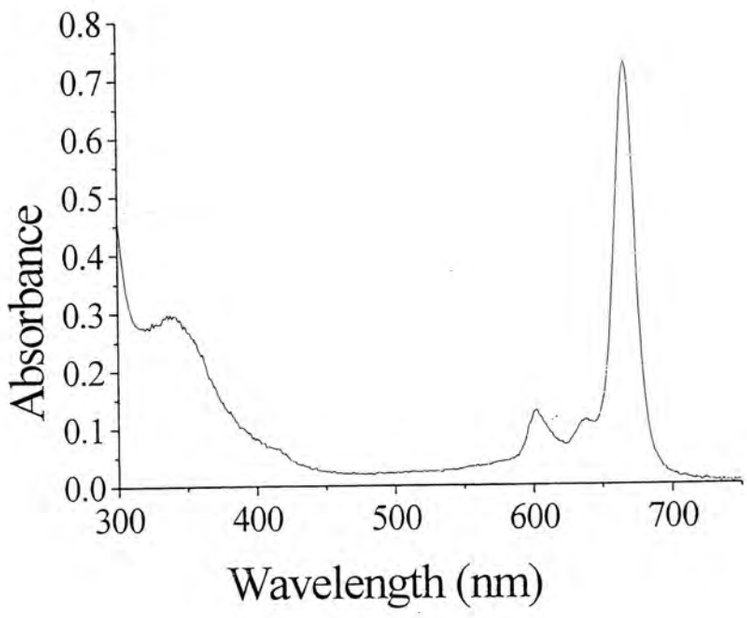


Figure 28. UV-Vis spectrum of **43** in THF; [**43**]: 2.9 mg in 10 cm^3 THF.

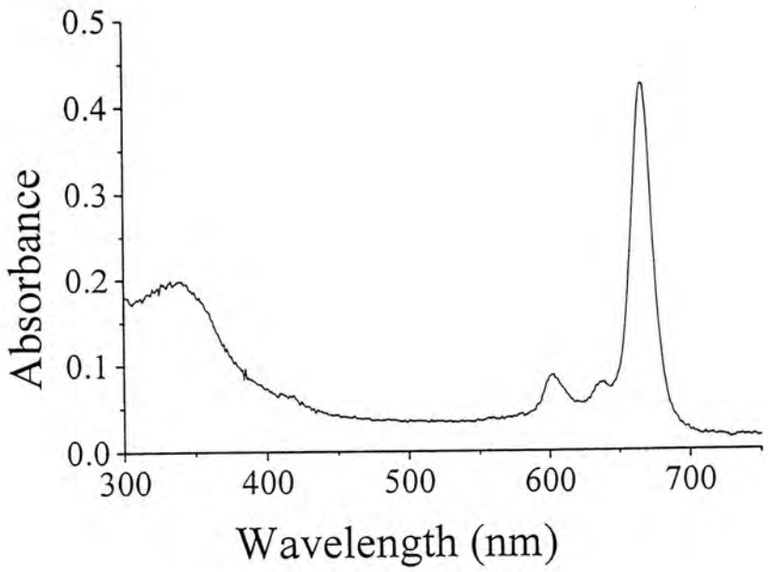


Figure 29. UV-Vis spectrum of **44** in THF; [**44**]: 2.7 mg in 10 cm^3 THF.

*2.2.2 Characterization of the Polymers **41 - 44***

All four polymers gave very similar NMR spectra to those of the respective polymers prepared from the tetrasubstituted phthalocyanine monomer **25**. Figures 30 and 31 show the ^1H and $^{13}C\{^1H\}$ NMR spectra of polymer **41**. The signals at *ca.* δ 5.4 and 5.2 in the ^1H NMR spectrum can be assigned to the *trans* and *cis* olefinic protons, respectively in *ca.* 5.1 : 1 ratio. The presence of *cis* and *trans* double bonds in the polymer backbone is also supported by the ^{13}C NMR spectrum which shows signals attributed to both configurations.

The ^1H and ^{13}C NMR spectra of **43** are also given in Figures 32 and 33. The signals at *ca.* δ 5.89 and 5.60 can be attributed to the *trans* and *cis* olefinic protons in *ca.* 1 : 1.2 ratio. The

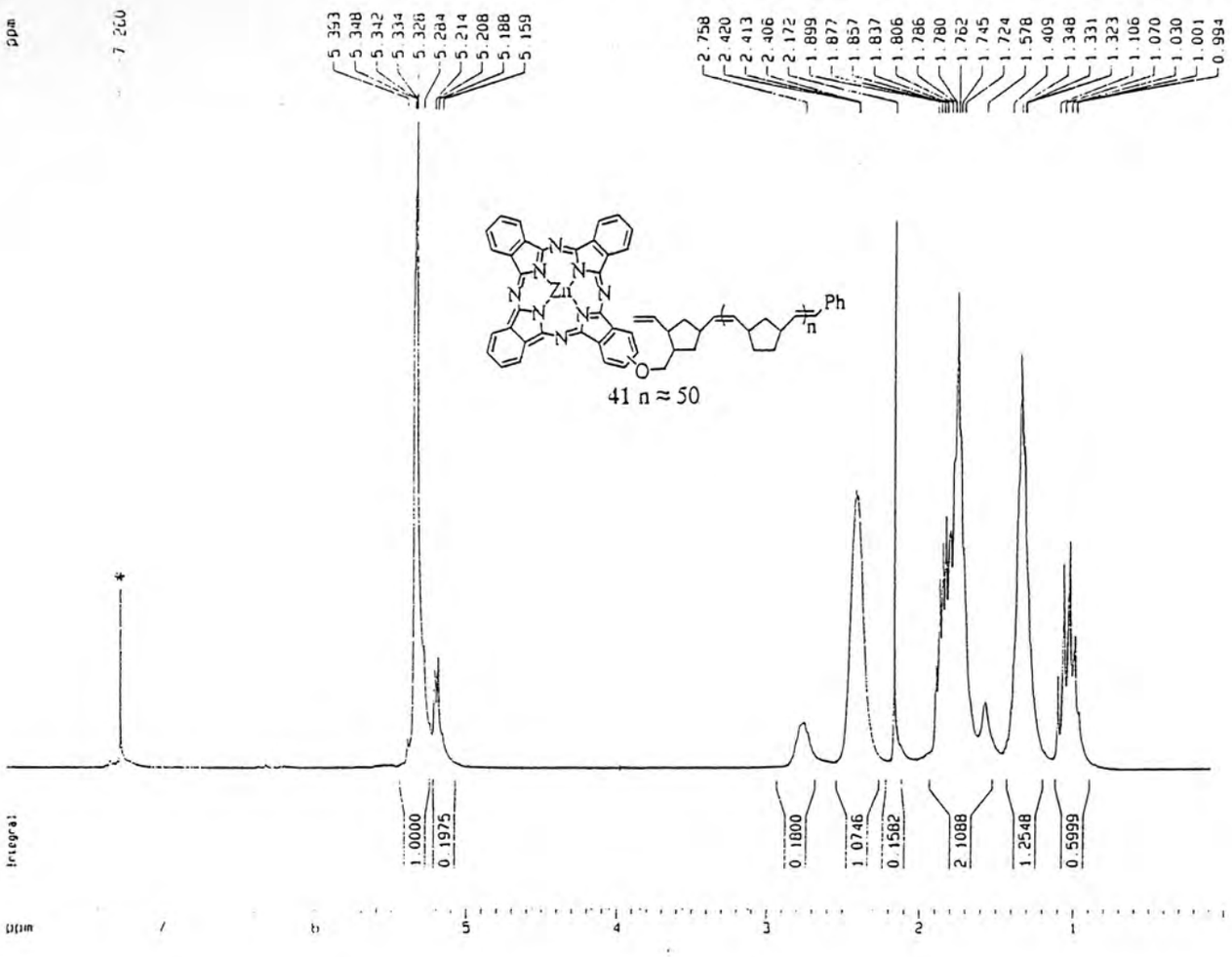


Figure 30. ^{1}H NMR spectrum of **41** in $CDCl_3$; * indicates the solvent peak.

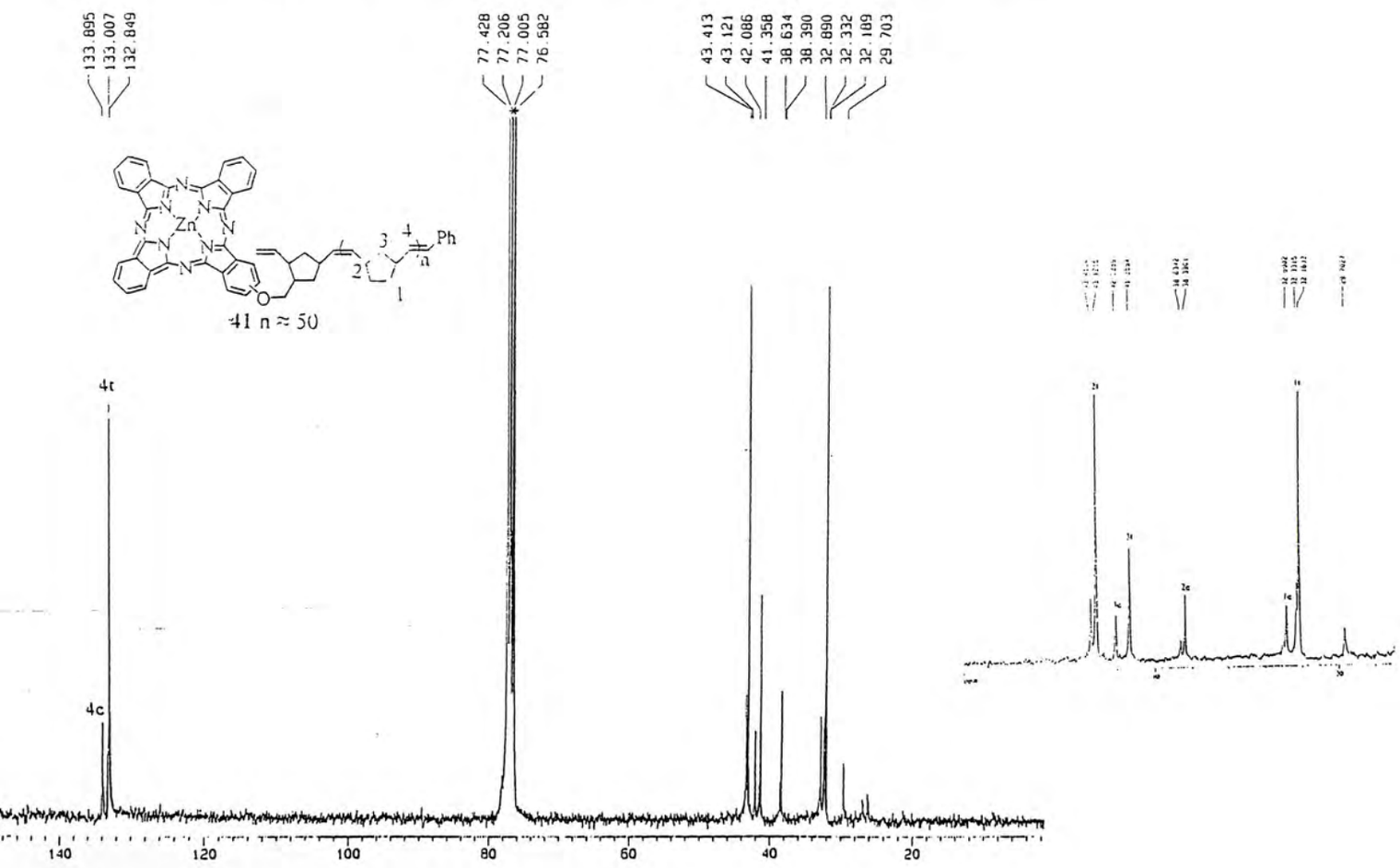


Figure 31. $^{13}C\{^{1}H\}$NMR spectrum of **41** in $CDCl_3$; * indicates the solvent peaks.

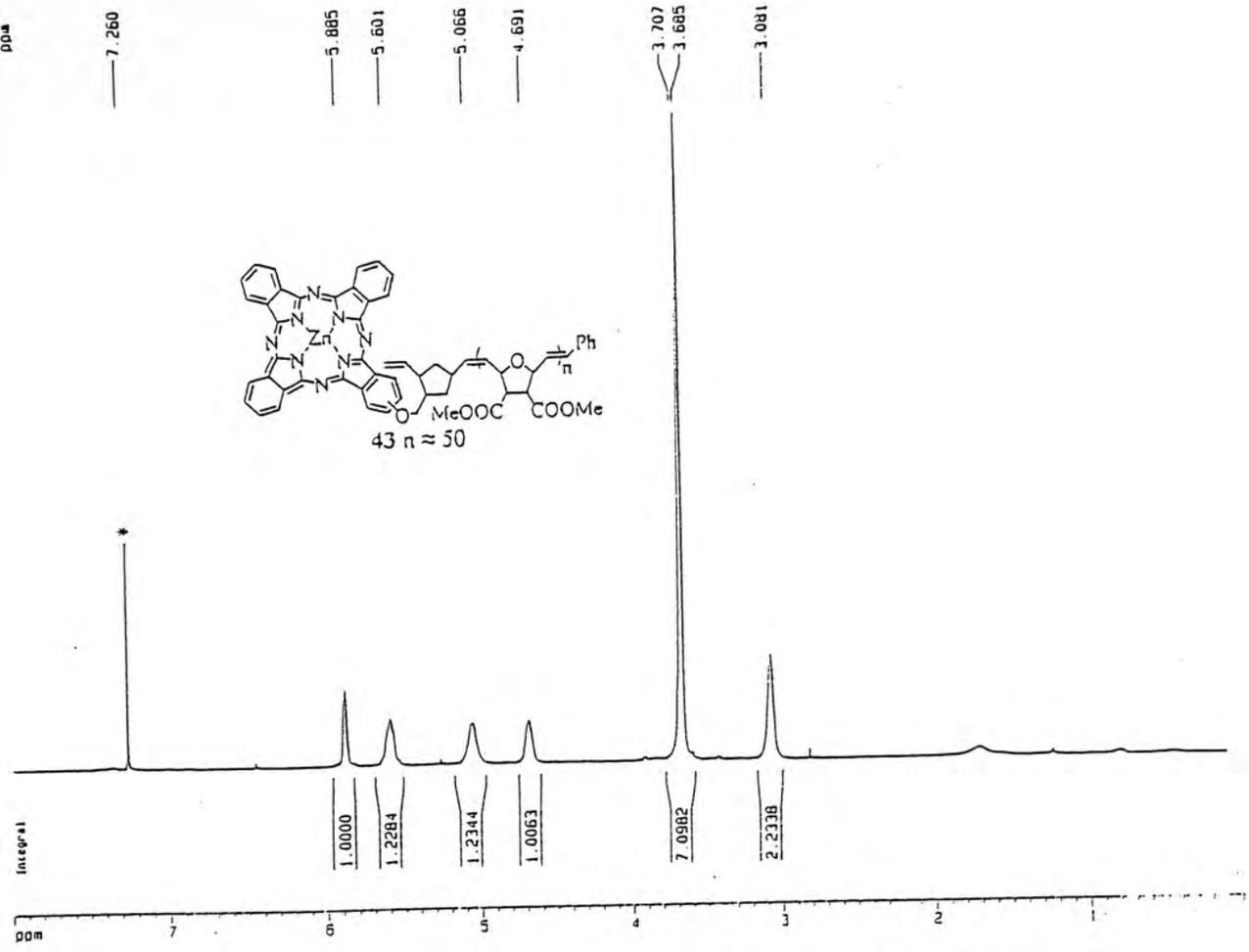


Figure 32. ^{1}H NMR spectrum of 43 in $CDCl_3$; * indicates the solvent peak.

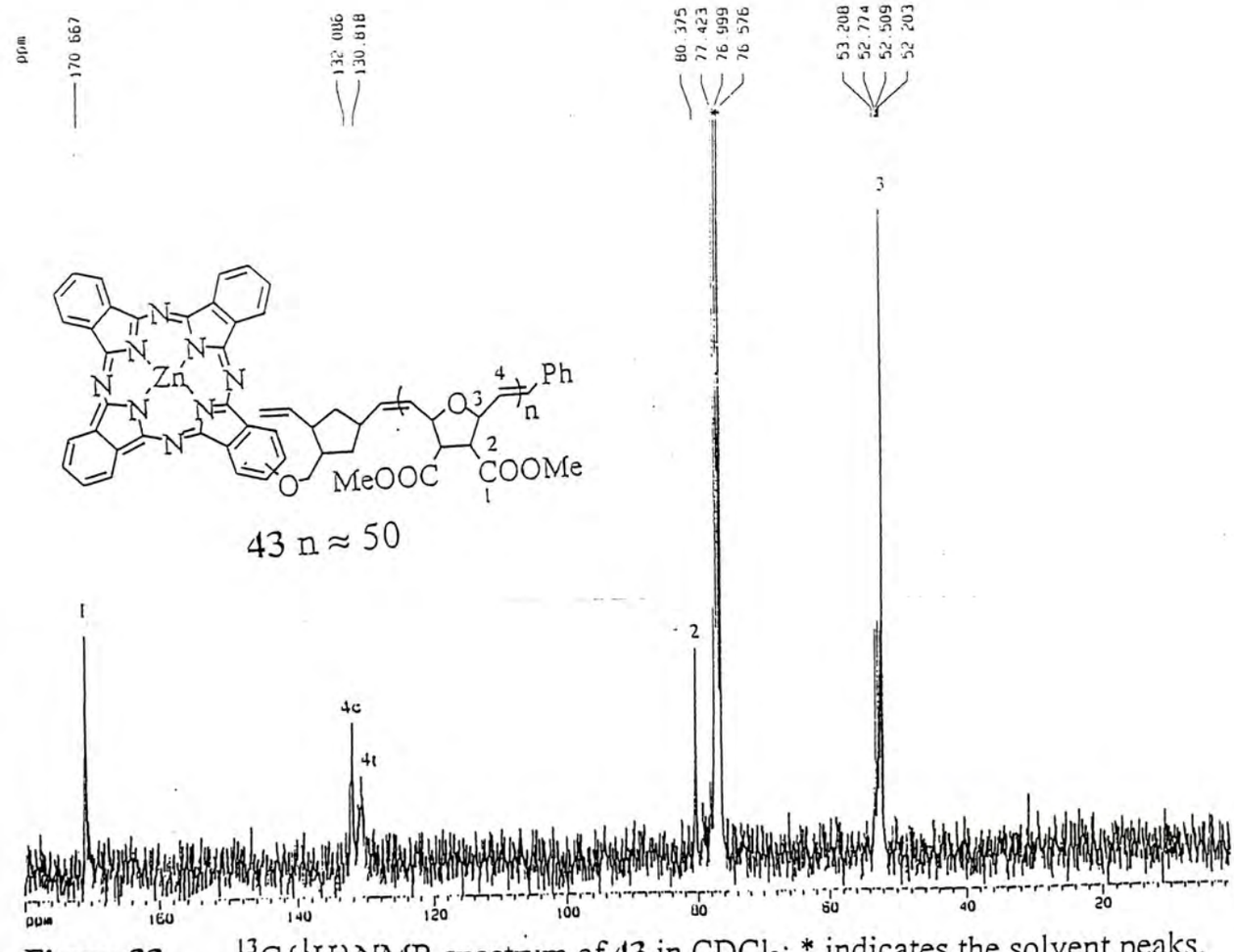


Figure 33. $^{13}C\{^{1}H\}$ NMR spectrum of 43 in $CDCl_3$; * indicates the solvent peaks.

The molecular weights of the polymers **41 – 44** were determined by a laser light scattering method. As shown in Table 5, the experimental data are in accord with the theoretical values based on the assumption that the polymers contain only one phthalocyanine linked to 50 or 100 equiv. of the repeating units.

	M_w (calcd)	M_w
41	5420	5660
42	10100	11900
43	11300	12400
44	21900	22300

Table 5. Molecular weights of the polymers **41 – 44**.

The fluorescence quantum yields of **41 – 44** were also determined and are given in Table 6, which also includes the data for the monomer **40** for comparison. The values are generally higher than those of the corresponding polymers generated from the tetrasubstituted phthalocyanine **25** (Table 3). This could be attributed to their lesser extent of cross-linking and aggregation as discussed in previous sections.

	Quantum yield
40	0.31
41	0.09
42	0.21
43	0.36
44	0.35

Table 6. Fluorescence quantum yields of the monomer **40** and polymers **41 – 44** in THF.

As phthalocyanines are well-known singlet oxygen generators which allow them to be used as photosensitizers, it will be interesting to examine how the polymer backbone affects the photosensitizing ability of the macrocycles. By using a steady-state method reported by Wöhrle *et al.*,[49] which employs 1,3-diphenylisobenzofuran (DPBF) as the $^1O_2$ quencher, we determined the singlet oxygen quantum yields (Φ_Δ) of the polymers **41 – 44** using the unsubstituted zinc phthalocyanine as the standard (0.56 in DMF). As shown in Table 7, all the values are substantially lower than the reference compound, in particular for 42 and 44, which have longer polymeric substituents. It is likely that a longer polymer chain may better shield the phthalocyanine core, hindering the approach of DPBF. As a result, the $^1O_2$ generated in the vicinity of phthalocyanine ring may be captured by the polymer chain giving a lower quantum yield.

	Singlet oxygen quantum yield
41	0.49
42	0.24
43	0.48
44	0.25

Table 7. Singlet oxygen quantum yields of **41** – **44**.

*2.2.2 Fluorescence Quenching of **40** and Polymers **41** – **44***

Since the polymers **41** – **44** are highly fluorescent, we investigated the fluorescence quenching of these polymers using 1,4-naphthaquinone as the quencher.[50] The concentration of **40** was about 5.34 X 10^{-5} Mol dm^{-3} and the concentration for the polymers were about 3.0 mg in 10 cm^3 THF. Figure 34 shows the Stern-Volmer plot for the fluorescence quenching of **44**, where I_o / I is the ratio of the original fluorescence intensity to the fluorescence intensity after the addition of 1,4-naphthaquinone. A straight line was obtained from which the quenching constant (K_{SV}) was found to be 3.27 X 10^4 $mol^{-1}dm^3$. The other three polymers and the monomer **40** behaved similarly and the results are tabulated in Table 8. It can be seen that the introduction of a poly(norbornene) chain decreases the rate of quenching.

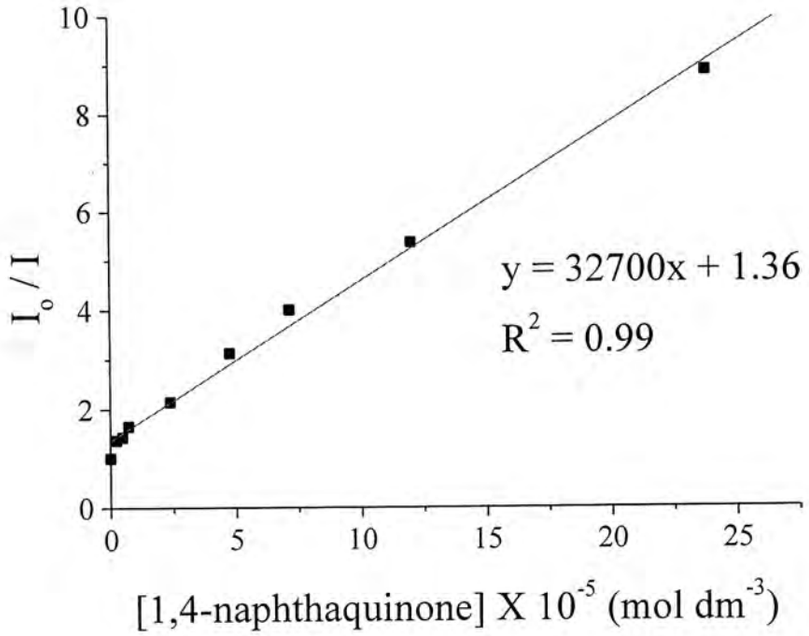


Figure 34. Stern-Volmer plot for fluorescence quenching of **44** in THF by 1,4-naphthaquinone

	Stern-Volmer Quenching Constant ($mol^{-1}dm^3$)
40	1.88 X 10^2
41	1.49 X 10^2
42	1.25 X 10^2
43	4.62 X 10^4
44	3.27 X 10^4

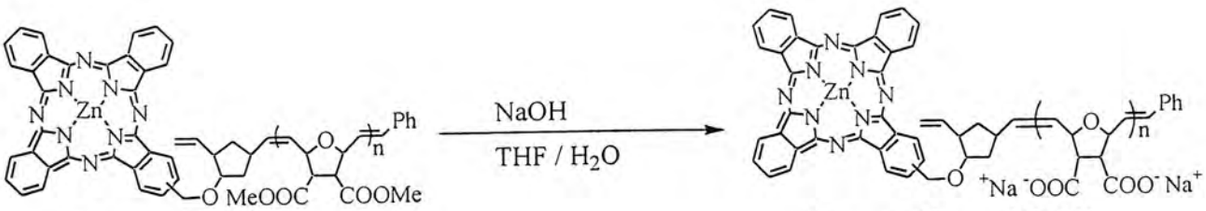
Table 8. Stern-Volmer Quenching Constants for **40** – **44** in THF using 1,4-naphthaquinone as the quencher.

2.2.4 *Preparation of Water-soluble Poly(7-oxanorbornene)*

Water-soluble phthalocyanines are of special importance because of their potential applications in photodynamic therapy,[51] photoinactivation of viruses,[52] and photocatalytic degradation of pollutants.[53] This class of macrocyclic compounds however has been relatively little studied.

Polymers **43** and **44**, which contain ester functionalities, can undergo alkaline hydrolysis to give the corresponding polycarboxylates (Scheme 22). The resulting green polymers are soluble in aqueous media and could be purified readily by washing with various organic solvents such as hexane and dichloromethane.

Scheme 22



43 n ≈ 50
44 n ≈ 100

45 n ≈ 50 (77 %)
46 n ≈ 100 (70 %)

Figures 35 and 36 show the UV-Vis spectra of **45** and **46** in diluted aqueous solutions. Both spectra show two broad absorptions at *ca.* 620 and 690 nm, showing that the phthalocyanine core exhibits a very high aggregation tendency. Since polymers **45** and **46** are not soluble in most organic solvents like methanol or DMSO, the solvent effects on the

aggregation tendency could not be investigated. As expected, no fluorescence was detected for these two polymers in aqueous media.

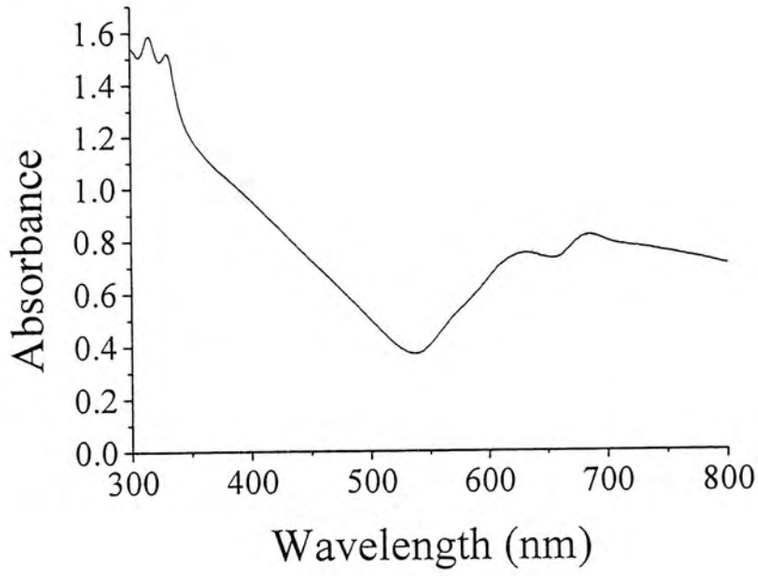


Figure 35. UV-Vis spectrum of **45** in H_2O; [**45**]: 3.2 mg in 10 cm^3 H_2O.

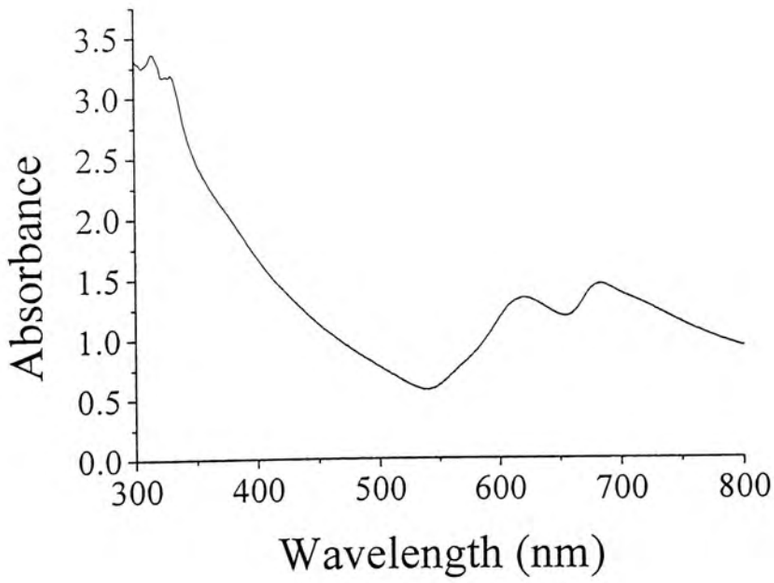


Figure 36. UV-Vis spectrum of **46** in H_2O; [**46**]: 3.3 mg in 10 cm^3 H_2O.

2.3 Conclusion

We have prepared two series of polymeric phthalocyanines. The first system contains a zinc(II) or palladium(II) phthalocyanine core substituted with four poly(norbornene) or poly(7-oxanorbornene) chains. Due to the cross-linking process, these polymers in particular the former, have lower solubility in common organic solvents, exhibiting a relatively high aggregation tendency, particularly, for the palladium system. The aggregation behavior together with the photophysical properties have been studied by steady state and transient absorption spectroscopy. Another series of phthalocyanine-containing polymer system contain a zinc(II) phthalocyanine core substituted with one poly(norbornene) or poly(7-oxanorbornene) chain. As shown by absorption spectroscopy, these polymers have higher solubility in organic solvents and lower aggregation tendency. Due to the potential application for photodynamic therapy, a water-soluble phthalocyanine-containing polymer with less aggregation will be a novel subject for further study.

3. EXPERIMENTAL SECTION

3.1 General Methods

Reactions were performed under an atmosphere of nitrogen. THF and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium oxide. *n*-Pentanol was distilled from sodium prior to use. DMF was dried over barium oxide and distilled under reduced pressure. Column chromatographic purifications were carried out on silica gel columns (Macherey-Nagel, 70-230 mesh) with the indicated eluents. All other reagents and solvents were of reagent grade and used as received.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 (^{1}H, 300; ^{13}C, 75.5 MHz) spectrometer with $CDCl_3$ as solvent unless otherwise stated. Spectra were referenced internally using the residual solvent (^{1}H: $CDCl_3$, δ 7.26) or solvent (^{13}C: $CDCl_3$, δ 77.0) resonances relative to $SiMe_4$. IR spectra were measured on a Nicolet Magna 550 spectrometer as KBr pellets. Electron Impact (EI) mass spectra were recorded on a HP 5989B spectrometer. Liquid secondary ion (LSI) mass spectra were measured on a Bruker APEX 47e ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

The theoretical yields of all the polymers were computed by calculating the ratio of the

polymer product with the sum of mass of the norbornene and the phthalocyanine with a benzylidene end-groups.

3.2 Photophysical Measurements

UV-Vis and steady-state fluorescence spectra were taken on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. The quantum yields were determined from the equation $\Phi_{sample} = (I_{sample}/I_{ref})(A_{ref}/A_{sample})(n_{sample}^2/n_{ref}^2)\Phi_{ref}$,[54] where I_{sample} and I_{ref} are the measured fluorescence (area under the fluorescence spectra) of the sample and the reference respectively, A_{sample} and A_{ref} are the absorbances of the sample and the reference, respectively, at the same excitation wavelength, n_{sample} and n_{ref} are the refractive index of the solvent used for the sample and the reference respectively, and Φ_{ref} is the quantum yield of the reference. For the determination of singlet oxygen quantum yields (Φ_Δ), the method reported by Wöhrle *et al.* was employed,[49] except that the absolute light intensity of our system was not determined. All measurements were referenced to unsubstituted ZnPc which has a Φ_Δ value of 0.56.

3.3 Synthesis of Phthalocyanines with Four Poly(norbornene) Substituents

***exo* and *endo* 5-Norbornene-2-methanol (23).**[55] To a solution of 5-norbornene-2-carbaldehyde **(22)** (180 mg, 1.47 mmol) in methanol (30 ml) was added sodium borohydride (300 mg, 7.35 mmol) at room temperature. The mixture was stirred for 30 min, then another batch of sodium borohydride (300 mg, 7.35 mmol) was added and the mixture was stirred at room temperature for a further 1 h. The solvent was then removed under reduced pressure and water (100 ml) was added. The solution was acidified by adding concentrated hydrochloric acid dropwise until the pH of the solution became 5. Then the solution was extracted with diethyl ether (3 x 50 ml) and the combined extracts were dried over anhydrous sodium sulfate. After removing the volatiles in vacuo, a colorless liquid was obtained (174 mg, 97 %). ^{1}H NMR ($CDCl_3$) δ 5.94-6.02 (m, 1H, =*CH*), 5.83-5.85 (m, 1H, =*CH*), 3.52-3.58 (m, 1H, -CH_2), 3.40-3.47 (m, 1H, -CH_2), 3.25-3.34 (m, 1H, -*CH*), 3.07-3.10 (t, J = 28.5 Hz, 1H, -CH_2), 2.67-2.82 (m, 1H, -CH_2), 2.17 (s, 1H, -CH_2), 1.64-1.72 (m, 1H, -CH_2), 1.32 (d, J = 7.8 Hz, 1H, -CH_2), 1.10-1.19 (m, 1H, -CH_2), 0.36-0.40 (m, 1H, -CH_2).

***exo* and *endo* 4-[(Bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalonitrile (24).** A mixture of 5-norbornene-2-methanol **(23)** (43 mg, 0.35 mmol), 4-nitrophthalonitrile (60 mg, 0.35 mmol), and potassium carbonate (190 mg, 1.37 mmol) in DMF (20 ml) was stirred at 80 °C for 6 h. The volatiles were removed under reduced pressure giving a brown residue which was subjected to chromatography using ethyl acetate-hexane (2:1 v/v) as eluent. The

yellow solid was recrystallized from methanol to give a white solid (51.9 mg 61 %, mp 105.8 - 106.5 °C). ^{1}H NMR ($CDCl_3$) δ 7.64 (t, *J* = 6.0 Hz, 1H, Ar-*H*), 7.21 (t, *J* = 3.0 Hz, 1H, Ar-*H*), 7.12 (t, *J* = 2.7 Hz, 1H, Ar-*H*), 6.08-6.14 (m, 1H, =*CH*), 5.89-5.86 (m, 1H, =*CH*), 4.05 (t, *J* = 6.3 Hz, 1H, -*OCH*), 3.87 (t, *J* = 9 Hz, 1H, -*OCH*), 3.73 (t, *J* = 6.0 Hz, 1H, -*OCH*), 3.58 (t, *J* = 9.0 Hz, 1H, -*OCH*), 2.96 (s, 1H, -*CH*), 2.78 (s, 1H, -CH_2), 2.49 (m, 1H, -*CH*), 1.85-1.88 (m, 1H, -*CH*), 1.45-1.53 (m, 1H, -CH_2), 1.19-1.33 (m, 1H, -CH_2), 0.59-0.55 (m, 1H, -CH_2). ^{13}C NMR ($CDCl_3$) δ 138.2, 137.1, 135.1, 131.8, 129.0, 125.2, 119.3, 117.3, 115.8, 106.9, 73.4, 49.5, 41.8, 38.2, 29.5, 21.4. MS (EI) for $C_{16}H_{14}N_2O$, *m/z* = 251. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N 11.19%. Found: C, 76.71; H, 5.61; N, 11.17%.

Tetra[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalocyaninatozinc(II) (25). A mixture of 4-[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalonitrile **(24)** (100 mg, 0.40 mmol) and zinc acetate (35 mg, 0.16 mmol) in dry *n*-pentanol (3 ml) was heated at 90 °C with stirring under nitrogen and then 3 drops of DBU was then added and the mixture was heated at 150 °C for 6 h. The volatiles were then removed under reduced pressure give a green residue which was chromatographed using THF-hexane (1:3 v/v) as eluent. The crude solid was dissolved in minimal THF and then precipitated with hexanes to afford a green solid (192 mg, 45 %). UV-Vis (THF) [λ_{max} nm (log ε)]: 676 (4.95), 611 (4.24), 337 (4.64). MS (LSI) for $C_{64}H_{56}N_8O_4Zn$, *m/z* = 1065. Anal. Calcd for $C_{64}H_{56}N_8O_4Zn$: C, 72.07; H, 5.29; N 10.51%. Found: C, 72.15; H, 6.13; N, 8.85%.

Tetra[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalocyaninatopalladium(II) (27). A mixture of 4-[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalonitrile **(24)** (100 mg, 0.40 mmol) and palladium acetate (48 mg, 0.16 mmol) in dry *n*-pentanol (3 ml) was heated at 90 °C with stirring under nitrogen and then 3 drops of DBU was then added and the mixture was heated at 150 °C for 6 h. After removing the volatiles under reduced pressure, the residue was chromatographed using THF as eluent. The crude solid was dissolved in minimal THF and then precipitated with hexanes twice to afford a green solid (124 mg, 28 %). UV-Vis (THF) [λ_{max} nm (log ε)]: 665 (5.00), 613 (4.67), 328 (4.80). Anal. Calcd for $C_{64}H_{56}N_8O_4Pd$: C, 69.40; H, 5.10; N 10.12%. Found: C, 69.16; H, 5.47; N, 9.06%.

Tetra(polynorbornenes)phthalocyaninatozinc(II) (29). To a solution of norbornene (105 mg, 1.117 mmol) in CH_2Cl_2 (1 ml) was added benzylidenebis(tricyclohexylphosphine)-dichlororuthenium(IV) **(17)** (69.8 mg, 0.085 mmol) in CH_2Cl_2 (1 ml) under nitrogen. The solution was stirred at room temperature for 1 h, then tetra[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalocyaninatozinc **(25)** (23 mg, 0.022 mmol) in CH_2Cl_2 (1 ml) was added. The mixture was stirred for a further 1 h then exposed to air for 15 min. The mixture was then added in dropwise to stirred methanol (50 ml) to induce precipitation of a green fibrous material which was dissolved in THF and reprecipitated in methanol for further purification. The resulting green polymer was dried in vacuum. Yield 85.1 mg (71 %). ^{13}C NMR ($CDCl_3$) δ 133.9, 133.0, 43.4, 42.1, 41.4, 38.4, 32.9, 32.2.

Tetra(polynorbornenes)phthalocyaninatozinc(II) (30). By using the above procedure, norbornene (96 mg, 1.021 mmol) and **25** (11.5 mg, 0.011 mmol) were treated with the catalyst **17** (34 mg, 0.041 mmol) to give a green solid. Yield 81.5 mg (69 %). ^{1}H NMR ($CDCl)_3$ δ 5.34 (m, -CH_2), 5.22 (d, -CH_2), 2.42 (s, -CH_2), 1.86 (m, -CH), 1.35 (m, -CH_2), 1.07 (m, -CH_2).

Tetra(polynorbornenes)phthalocyaninatopalladium(II) (31). To a solution of norbornene (75 mg, 0.798 mmol) in CH_2Cl_2 (1 ml) was added the catalyst **17** (52.8 mg, 0.064 mmol) in CH_2Cl_2 (1 ml) under nitrogen. The solution was stirred at room temperature for 1 h, then tetra[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalocyaninatopalladium(II) **(27)** (17.7 mg, 0.016 mmol) in CH_2Cl_2 (5 ml) was added. The mixture was stirred at 60 °C for further 6 h then exposed to air for 15 min. The resulting mixture was poured slowly into stirred methanol (50 ml) to give a green solid which was dissolved in THF and reprecipitated in methanol for further purification. The resulting green solid was dried in vacuum. Yield 33.8 mg (45 %). ^{1}H NMR ($CDCl_3$) δ 5.33-5.39 (m, =CH_2), 5.20 (d, J = 1.5 Hz, =CH_2), 2.41 (s, -CH_2), 1.76-1.86 (m, -CH), 1.35-1.39 (m, -CH_2), 1.22-1.25 (m, -CH_2)

Tetra(polynorbornenes)phthalocyaninatopalladium(II) (32). According to the above procedure, norbornene (99.3 mg, 1.056 mmol) and monomer **27** (12.2 mg, 0.011 mmol) were treated wth the catalyst **17** (34.9 mg, 0.042 mmol) to give a green solid. Yield 39.7 mg (40 %). ^{13}C NMR δ 133.9, 129.8, 43.1, 42.1, 41.4, 38.4, 32.8, 32.2, 29.7.

***exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (33).**[33] Furan (10 ml, 0.142 mmol) was added to a solution of maleic anhydride (12.2 g, 0.142 mol) in dry THF (20 ml). The mixture was stirred until all the maleic anhydride dissolved in THF to give a pale yellow solution. The solution was allowed to stand for 24 h at room temperature to give yellow crystals which were collected by suction filtration and washed with cold THF. The resulting white solid was dried in vacuum. Yield 14.8 g (63 %). ^{1}H NMR ($CDCl_3$) δ 6.56 (s, 2H, =*CH*), 5.43 (s, 2H, -*OCH*), 3.17 (s, 2H, -*COCH*).

***exo,exo*-5,6-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene (34).**[33] To a solution of *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **(33)** (5 g, 0.030 mol) in methanol (10 ml) was added concentrated hydrochloric acid (1 ml) in dropwise. The flask was swirled between drops. Then the flask was fitted with a reflux condenser and heated to reflux for 2 h. During the heating, all the solid was dissolved. After heating, the reaction mixture was cooled to room temperature, then immersed in an ice bath to induce crystal formation. The white solid formed was collected by suction filtration, washed with cold methanol, and dried in vacuum. Yield 3.13 g (49 %). ^{1}H NMR ($CDCl_3$) δ 6.42 (s, 2H, =*CH*), 5.22 (s,. 2H, -*OCH*), 3.66 (s, 2H, Me), 2.78 (s, 2H, -*COCH*).

Tetra{poly[*exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene]}phthalocyaninatozinc(II) (36). According to the procedure used for prepare **29**, *exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene **(34)** (152 mg, 0.717 mmol)

and **25** (14.1 mg, 0.014 mmol) were polymerized using benzylidenebis(tricyclohexyl-phosphine)dichlororuthenium(IV) **(17)** (47.3 mg, 0.057 mmol) as the catalyst to give a green polymeric material. Yield 66.6 mg (67 %). ^{1}H NMR ($CDCl_3$) δ 5.89 (s, -CH_2), 5.60 (s, -CH_2), 5.06 (s, -OCH_2), 4.69 (s, -OCH_2), 3.69 (s, -CH_2), 3.08 (s, -CH_2).

Tetra{poly[*exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene]}phth-a locyaninatozinc(II) (37). By using the above procedure, monomer **34** (120 mg, 0.566 mmol) and **25** (5.9 mg, 0.006 mmol) were treated with the catalyst **17** (19.8 mg, 0.024 mmol) to give a green polymer material. Yield 75.6 mg (63 %). ^{1}H NMR ($CDCl_3$) δ 5.89 (s, -CH_2), 5.60 (s, -CH_2), 5.06 (s, -OCH_2), 4.69 (s, -OCH_2), 3.69 (s, -CH_2), 3.08 (s, -CH_2).

Tetra{poly[*exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene]}phth-a locyaninatopalladium(II) (38). By using the above procedure, monomer **34** (125 mg, 0.570 mmol) and **27** (12.6 mg, 0.011 mmol) were treated with the catalyst **17** (37.1 mg, 0.045 mmol) to give a green polymer material. Yield 52.5 mg (42 %). ^{13}C NMR ($CDCl_3$) δ 170.9, 132.1, 130.9, 80.4, 53.2, 52.2.

Tetra{poly[*exo,exo*-5,6-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene]}phth-a locyaninatopalladium(II) (39). By using the above procedure, monomer **34** (101 mg, 0.476 mmol) and **27** (5.27 mg, 0.005 mmol) were treated with the catalyst **17** (17.3 mg, 0.021 mmol) to give a green polymer material. Yield 49.5 mg (49 %). ^{1}H NMR ($CDCl_3$) δ 5.88 (s, -CH_2), 5.59 (s, -CH_2), 5.06 (s, -OCH_2), 4.69 (s, -OCH_2), 3.69 (s, -CH_2), 3.08 (s, -CH_2).

3.4 Synthesis of Phthalocyanines with One Poly(norbornene) Substituent

2-[(Bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalocyaninatozinc(II) (40). 4-[(Bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalonitrile **(24)** (100 mg, 0.40 mmol), 1,2-dicyanobenzene (1.03 g, 8.05 mmol), and zinc acetate (140 mg, 0.64 mmol) in dry *n*-pentanol (10 ml) were heated at 90 °C with stirring under nitrogen and then 3 drops of DBU was then added and the mixture was heated at 150 °C for further 6 h. Upon cooling to room temperature, *n*-pentanol was evaporated under reduced pressure and the residue was passed through a silica gel column using ethyl acetate-hexane (2:1 v/v) as eluent. The solid was dissolved in minimal THF and then precipitated with hexanes to afford a green product (83.9 mg, 32 %). UV-Vis (THF) [λ_{max} nm (log ε)]: 665 (4.95), 601 (4.13), 341 (4.38). MS (LSI) for $C_{40}H_{26}N_8OZn$, m/z = 699.

2-(Polynorbornene)phthalocyaninatozinc(II) (41). To a solution of norbornene (99 mg, 1.053 mmol) in CH_2Cl_2 (1 ml) was added benzylidenebistricyclohexylphosphine)-dichlororuthenium(IV) **(17)** (17 mg, 0.021 mmol) in CH_2Cl_2 (1 ml) under nitrogen. The solution was stirred at room temperature for 1 h, then 2-[(bicyclo[2.2.1]hept-2-enyl)-5′-methoxy]phthalocyaninatozinc **(40)** (12 mg, 0.017 mmol) in CH_2Cl_2 (5 ml) was added. The mixture was refluxed for further 3 h then exposed to air for 15 min. The resulting mixture was poured slowly into stirred methanol (50 ml) to give a green solid which was dried in vacuum. Yield 58 mg (56 %). ^{1}H NMR ($CDCl_3$) δ 5.33-5.39 (ml

=CH_2), 5.16-5.21 (m, =CH_2), 2.41 (s, -CH_2), 1.84 (m, -CH), 1.32-1.35 (m, -CH_2), 0.99-1.10 (m, -CH_2). ^{13}C NMR ($CDCl_3$) δ 133.9, 132.8, 43.4, 42.1, 41.4, 38.6, 32.9, 32.3, 29.7.

2-(Polynorbornene)phthalocyaninatozinc(II) (42). According to the above procedure, norbornene (97 mg, 1.032 mmol) and **40** (6 mg, 0.008 mmol) were treated with the catalyst **17** (9 mg, 0.010 mmol) to give a green product. Yield 64 mg (69 %). ^{1}H NMR ($CDCl)_3$ δ 5.39 (m, =CH_2), 5.19 (d, =CH_2), 2.43 (s, -CH_2), 1.86 (m, -CH), 1.39 (m, -CH_2), 1.07 (m, -CH_2). ^{13}C NMR ($CDCl_3$) δ 133.9, 133.0, 43.4, 42.1, 41.4, 38.4, 32.9, 32.3.

2-{Poly[*exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene]}phthalocyaninatozinc(II) (43). According to the above procedure, *exo,exo*-5,6-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene **(34)** (122 mg, 0.575 mmol) and **40** (6 mg, 0.009 mmol) were treated with the catalyst **17** (9 mg, 0.010 mmol) to give a green product. Yield 50.2 mg (52 %). ^{1}H NMR ($CDCl_3$) δ 5.89 (s, -CH_2), 5.60 (s, -CH_2), 5.07 (s, -OCH_2), 4.69 (s, -OCH_2), 3.69 (s, -CH_2), 3.08 (s, -CH_2). ^{13}C NMR ($CDCl_3$) δ 170.7, 132.1, 130.8, 80.4, 53.2, 52.5.

2-{Poly[*exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene]}phthalocyaninatozinc(II) (44). According to the above procedure, *exo,exo*-5,6-Bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene **(34)** (128 mg, 0.604 mmol) and **40** (3 mg, 0.005 mmol) were treated with the catalyst **17** (5 mg, 0.006 mmol) to give a green product. Yield 52.5 mg (57 %). ^{1}H NMR ($CDCl_3$) δ 5.89 (s, -CH_2), 5.60 (s, -CH_2), 5.06 (s,

-OCH_2), 4.69 (s, -OCH_2), 3.69 (s, -CH_2), 3.08 (s, -CH_2).

Sodium 2-{poly[*exo,exo*-5,6-bis(carboxylato)-7-oxabicyclo[2.2.1]hept-2-ene-]}phthalocyaninatozinc(II) (45). Polymer **43** (60 mg) was dissolved in THF (10 ml) to give a green solution. Sodium hydroxide (0.80 g) was dissolved in de-ionized water (10 ml), then the solution was added dropwise to the green solution of **43**. Some green precipitates formed after about 15 min. The solution was stirred for 4 h at ambient temperature to give green precipitates which were filtered, washed with hexane and dichloromethane, and dried in vacuum Yield 46 mg (77 %).

Sodium 2-{poly[*exo,exo*-5,6-bis(carboxylato)-7-oxabicyclo[2.2.1]hept-2-ene-]}phthalocyaninatozinc(II) (46). Using the above procedure, polymer **44** (60 mg) was hydrolyzed to give the water soluble polymer **46**. Yield 42 mg (70 %).

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